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CONTENTS

RP	TITLE AND AUTHOR	Page
1631.	Method for calculating the properties of hydrocarbons and its application to the refractive indices, densities, and boiling points of the paraffin and monoolefin hydrocarbons. William J. Taylor, Joan M. Pignocco, and Frederick D. Rossini.....[Price 10 cents]	413
1632.	Separation and determination of aromatic and monoolefin hydrocarbons in mixtures with paraffins and naphthenes by adsorption. Beveridge J. Mair.....[Price 10 cents]	435
1633.	Methods for the evaluation of analytical filter papers. B. W. Scribner and W. K. Wilson.....[Price 5 cents]	453
1634.	Intrinsic viscosities and osmotic molecular weights of cellulose acetate fractions. Arnold M. Sookne and Milton Harris.....[Price 5 cents]	459
1635.	Polymolecularity and mechanical properties of cellulose acetate. Arnold M. Sookne and Milton Harris .....[Price 5 cents]	467

The articles listed may be purchased separately (see cover page II) at the prices stated

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1651

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METHOD FOR CALCULATING THE PROPERTIES OF HYDROCARBONS AND ITS APPLICATION TO THE REFRACTIVE INDICES, DENSITIES, AND BOILING POINTS OF THE PARAFFIN AND MONOOLEFIN HYDROCARBONS [1]

By William J. Taylor,[2] Joan M. Pignocco,[2] and Frederick D. Rossini

ABSTRACT

A method is described for calculating the properties of hydrocarbons which involves the summation of contributions from component parts of the molecule, together with contributions from interactions between adjacent component parts.

For the paraffin hydrocarbons, the calculations were made in terms of the difference in the value of the property between a given normal paraffin and its isomers, and the required constants were evaluated from data on 33 paraffins, C_5 to C_8. For these paraffins, the average deviation of the calculated from the experimental values is ± 0.00074 g/ml in density, ± 0.00042 in refractive index (n_D at 20° C), and ± 0.55° C in the normal boiling point.

In the case of the monoolefin hydrocarbons, the calculations were made in terms of the difference in the value of the property between a given monoolefin and the corresponding paraffin having the same carbon skeleton, and the required constants were evaluated from data on 58 monoolefins, C_5 to C_7. For these monoolefins, the average deviation of the calculated from the experimental values is ± 0.0031 g/ml in density, ± 0.0020 in refractive index (n_D at 20° C), and ± 1.33° C in the normal boiling point.

CONTENTS

		Page
I.	Introduction	413
II.	General method	414
III.	Application to paraffin hydrocarbons	417
IV.	Application to monoolefin hydrocarbons	426
V.	Discussion	434
VI.	References	434

I. INTRODUCTION

In connection with the work of the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons," at the National Bureau of Standards, it became necessary to make selections of values of the physical properties of refractive index, density, and normal boiling point for

[1] This investigation was performed at the National Bureau of Standards by the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons."

[2] Research Associate on the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

several nonanes and octenes for which no data whatever were available and for several other nonanes and octenes for which the existing data appeared to be rather uncertain. This paper describes the method by which these caculations were made.

It has long been known that the properties of hydrocarbons vary more or less regularly with their molecular structure, and numerous correlations of various properties of hydrocarbons have been made. These include, for example, the graphical methods used by Calingaert and coworkers in connection with molecular volume [1, 2],[1] the structural increment method of Francis in connection with refractive index, density, and normal boiling point [3, 4], and the theoretical method used by Huggins in connection with density and refractive index [5, 6]. The present investigation follows more nearly the method of Huggins [5] in that, from known values for a considerable number of compounds of a given type, certain constants are evaluated whose appropriate summation permits evaluation of the property for a given hydrocarbon of the same type, with the number of times a given constant is added being determined entirely by the structure of the given molecule.

II. GENERAL METHOD

It is frequently desired to correlate a particular property of a group of compounds by fitting an assumed function containing adjustable parameters to the observed values of the property. In the simple case of one independent variable, as the number of carbon atoms in a homologous series of compounds, the method of least squares is often used in the adjustment of the parameter. If the group of compounds is less simply related than a homologous series it is usually necessary to introduce more than one independent variable in order to represent the data adequately.

The advantages of the method of least squares in the multi-dimensional case are essentially the same as in the one dimensional case, namely, the method presents a unique set of values for the parameters based on all the data. In addition, the use of least squares is a relatively rapid method when there are several independent variables, since other methods become increasingly difficult.

The method of least squares is nothing more than a mathematical procedure for minimizing the sum of the squares of the residuals, or the differences between the observed values and the values calculated from the assumed function. These residuals may arise in two ways: (1) the observed values may be in error; (2) the true values will not, in general, satisfy the assumed function perfectly because of the approximate nature of the latter. The relative importance of these two factors depends upon the accuracy of the data and the correctness of the assumed function. If the first effect is predominant, the correlation is essentially a smoothing of the data, and the justification for using least squares is well known. If the second effect is predominant, the correlation is incapable of improving the data, and the interest then is attached to the values of the parameters, which may be used, for example, to calculate approximate values of the property for compounds for which it is unknown. In this case, the justification for the use of least squares is less clear, because the deviation of the true

[1] Figures in brackets indicate the literature references at the end of this paper.

values from the assumed function is not likely to follow a normal error curve. However, even in this case, a better criterion for the adjustment of the parameters than the minimization of the sum of the squares of the residuals does not seem to be available.

In the applications of least squares to be made here, the independent variables will be free of error, and the normal equations may then be derived very simply.[4] The derivation will be repeated briefly here in order to introduce the notation adopted and to make certain features of the procedure clear. The language of the physical problem at hand will be used for concreteness.

In a group of m compounds, let the observed value of a given property G be G_i for the ith compound. It is desired to represent G by a function of v independent variables $z_1, \ldots, z_v$, and t adjustable parameters $a_1, \ldots, a_t$

$$F=F(z_1, \ldots, z_v; a_1, \ldots, a_t). \tag{1}$$

The variables $z_1, \ldots, z_v$, are numbers known from the structure of the molecule, for example, the number of atoms or bonds of a given kind; let their values for the ith compound be $z_{1i}, \ldots, z_{vi}$. The parameters $a_1, \ldots, a_t$ are to be adjusted to minimize the sum of the weighted squares of the residuals, ϕ^2,

$$\phi^2=\sum_{i=1}^{i=m} w_i(G_i-F_i)^2. \tag{2}$$

The assignment of weights, w_i to the observed values G_i, will be discussed later. Setting the derivatives of ϕ^2 with respect to $a_1, \ldots, a_t$, equal to zero yields t equations

$$\sum_{i=1}^{i=m} w_i \frac{\partial F_i}{\partial a_s}(G_i-F_i)=0 \qquad (s=1, \ldots, t). \tag{3}$$

In general, eq 3 are not linear in $a_1, \ldots, a_t$. Let the (unknown) values of the parameters that satisfy eq 3 be $a_1, \ldots, a_t$, and assume that in some way approximate values $\bar{a}_1, \ldots, \bar{a}_t$, have been estimated. Then, neglecting second derivatives of F,

$$F=\overline{F}+\sum_{r=1}^{r=t} \overline{\frac{\partial F}{\partial a_r}}(a_r-\bar{a}_r)+ \ldots \tag{4a}$$

$$\frac{\partial F}{\partial a_s}=\overline{\frac{\partial F}{\partial a_s}}+ \ldots \qquad (s=1, \ldots, t), \tag{4b}$$

where $\overline{F}$ and $\overline{\partial F/\partial a_s}$ are to be evaluated at $a_1=\bar{a}_1, \ldots, a_t=\bar{a}_t$. Introducing eq 4 into eq 3, there is obtained

$$\sum_{r=1}^{r=t}(a_r-\bar{a}_r)\left[\sum_{i=1}^{i=m} w_i \overline{\frac{\partial F_i}{\partial a_r}}\overline{\frac{\partial F_i}{\partial a_s}}\right] \cong \sum_{i=1}^{i=m} w_i \overline{\frac{\partial F_i}{\partial a_s}}(G_i-\overline{F}_i) \qquad (s=1, \ldots, t). \tag{5}$$

[4] For a more general treatment, and for a method of solving the normal equations, see reference [7, chapters IV, VIII, and IX].

Equations 5 are the t normal equations, linear in $(a_1-\bar{a}_1), \ldots, (a_t-\bar{a}_t)$. After solving for the latter, $a_1, \ldots, a_t$ may be calculated. The final values of $a_1, \ldots, a_t$, will be essentially independent of $\bar{a}_1, \ldots, \bar{a}_t$, provided the latter are reasonably good estimates.

In the correlations described in this paper, F has the simple linear form

$$F=\sum_{r=1}^{r=t} a_r z_r; \quad \frac{\partial F}{\partial a_s}=z_s \qquad (s=1, \ldots, t), \tag{6}$$

and the normal equations become

$$\sum_{r=1}^{r=t} (a_r-\bar{a}_r) \sum_{i=1}^{i=m} w_i z_{ri} z_{si} = \sum_{i=1}^{i=m} w_i z_{si} (G_i-\bar{F}_i) (s=1, \ldots, t), \tag{7}$$

where

$$\bar{F}=\sum_{r=1}^{r=t} \bar{a}_r z_r. \tag{8}$$

For this form of F the normal equations are exact, so that solution of eq 7 yields the correct values of $a_1, \ldots, a_t$, no matter how inaccurate are the estimates $\bar{a}_1, \ldots, \bar{a}_t$. In particular, if $\bar{a}_1=0, \ldots, \bar{a}_t=0$, then, also, $\bar{F}=0$, and the normal equations become

$$\sum_{r=1}^{r=t} a_r \sum_{i=1}^{i=m} w_i z_{ri} z_{si} = \sum_{i=1}^{i=m} w_i z_{si} G_i (s=1, \ldots, t). \tag{9}$$

It may still be advantageous to make estimates $\bar{a}_1, \ldots, a_t$, and use eq 7 rather than eq 9, in order to reduce the number of significant figures necessary in the calculations.

After the solution of the normal equations for the parameters $a_1, \ldots, a_t$, the individual deviations, (G_i-F_i), may be calculated. For each correlation in this paper there are given one or more of the following: (1) the maximum deviation, or the maximum absolute value of (G_i-F_i); (2) the average deviation defined by

$$\text{Average deviation}=\frac{1}{m}\sum_{i=1}^{i=m} w_i|G_i-F_i|; \tag{10}$$

and (3) the standard deviation of a single value, σ, defined by

$$\sigma=\left[\frac{1}{m}\sum_{i=1}^{i=m} w_i (G_i-F_i)^2\right]^{1/2} \tag{11}$$

The assignment of weights, w, to the observed values of the property G is not an easy problem. If the uncertainty of the observed value for a given compound is considerably larger than the expected deviation of the true value from the calculated value, a low weight may be assigned to the value for this compound. However there is no justification for assigning a low weight to an accurate value which differs greatly from the calculated value, for the fault lies then with

the assumed function F, rather than with the data. In the correlations described in this report, a single value was first selected for each compound by suitable weighting of the experimental values for each compound; the correlation was then based on these selected values, assigning unit weight ($w=1$) to each compound included in the correlation.

III. APPLICATION TO PARAFFIN HYDROCARBONS

In the application of the present method to the paraffin hydrocarbons, there are several ways in which constants may be assigned to the component parts of the molecule and their interactions. Some of these will be discussed, in the order of increasing complexity.

One of the simplest schemes for the calculation of the properties of the paraffin hydrocarbons, C_nH_{2n+2} (where n is the number of carbon atoms), is the assignment of constants a_C and a_H for the contributions of carbon and hydrogen atoms, respectively, to the property G. The resulting equation for G is [5]

$$G=2a_H+(a_C+2a_H)n. \tag{12}$$

An alternative is the assignment of constants a_{CC} and a_{CH} for the contributions of carbon-carbon and carbon-hydrogen bonds, respectively to G. The equation for G is then

$$G=(2a_{CH}-a_{CC})+(a_{CC}+2a_{CH})n. \tag{13}$$

If the contributions of both bonds and atoms are included, the equation for G is the sum of the right sides of eq 12 and 13.

It follows that in each of these cases G takes the form

$$G=b_0+nb, \tag{14}$$

so that there are only two adjustable constants. It is also clear that the calculated value of G will be the same for all isomers, since n is the same for isomers.

Perhaps the simplest scheme that is capable of distinguishing isomeric paraffins is the assignment of constants for the contribution to G, of CH_3, CH_2, CH, and C groups, in which the carbon atom is, respectively, primary, secondary, tertiary, and quaternary. Let these constants be a_1, a_2, a_3, and a_4, and let the number of groups of each kind in the ith paraffin be z_{1i}, z_{2i}, z_{3i}, and z_{4i}, respectively. The equation for G_i is

$$G_i=z_{1i}a_1+z_{2i}a_2+z_{3i}a_3+z_{4i}a_4. \tag{15}$$

It is easily seen that the following relations exist between the z's and n, the total number of carbon atoms:

$$z_{1i}+z_{2i}+z_{3i}+z_{4i}=n_i. \tag{16}$$

$$3z_{1i}+2z_{2i}+z_{3i}=2n_i+2. \tag{17}$$

[5] Hereafter G will be used to represent both the observed value of the property and the function that represents the property. The meaning intended will always be clear from the context. In section II the property is represented by G and the function by F.

On substitution for z_{1i} and z_{2i} from eq 16 and 17, G takes the form

$$G_i=(2a_1-2a_2)+n_ia_2+z_{3i}(a_1-2a_2+a_3)+z_{4i}(2a_1-3a_2+a_4). \quad (18)$$

Denoting by G_n the value of G for the normal paraffin with the same value of n, eq 18 reduces to

$$G_n=(2a_1-2a_2)+n_ia_2. \quad (19)$$

Finally, there is obtained for the difference in the value of G between the isomer and the normal paraffin

$$\Delta G_i=(G_i-G_n)=z_{3i}(a_1-2a_2+a_3)+z_{4i}(2a_1-3a_2+a_4). \quad (20)$$

Equation 20 has been fitted by least squares (see also section II) to the increment of molal volume at 20°C, ΔV^{20}, to the increment of molal refraction for the D line at 20°C, $\Delta R_D{}^{20}$, and to the increment of the normal boiling point in degrees, centigrade, ΔBP_{760} for the 29 branched paraffins (1 pentane, 4 hexanes, 8 heptanes, and 16 octanes) normally liquid at 20°C (this excludes the gas, 2,2-dimethylpropane and the solid 2,2,3,3-tetramethylbutane). The data for the calculation of ΔV^{20}, $\Delta R_D{}^{20}$, and ΔBP_{760} were taken from the selected "best" values of these properties in the tables of the American Petroleum Institute Research Project 44, as of December 31, 1942. The reference values for the normal paraffins are given in table 1, and the difference between the values for the branched paraffins (isoparaffins) and the corresponding normal paraffins are given in table 2. The molal volume, V^{20}, and the molal refraction, $R_D{}^{20}$, are related to the molecular weight, M, the density at 20°C, d^{20}, and the refractive index for the D line at 20°C, $n_D{}^{20}$, by the equation

$$V^{20}=M/d^{20}. \quad (21)$$

$$R_D{}^{20}=\frac{M}{d^{20}}\left[\frac{(n_D{}^{20})^2-1}{(n_D{}^{20})^2+2}\right]. \quad (22)$$

TABLE 1.—*Reference values for the normal paraffins*

Compound	Density at 20° C	Refractive index at 20° C	Boiling point at 760 mm
	g/ml	n_D	*° C*
n-Pentane	0.6263	1.3576	36.07
n-Hexane	.6594	1.3750	68.74
n-Heptane	.6837	1.3877	98.42
n-Octane	.7026	1.3975	125.66
n-Nonane	.7178	1.4055	150.77

TABLE 2.—*Experimental and calculated values of the difference, between each of 29 isoparaffins, C_5 to C_8, and the corresponding normal paraffin, of the density, d, at 20° C, the molal volume, V, at 20° C, the refractive index, n_D, at 20° C, the molal refraction,[a] R_D, at 20°C, and the boiling point, BP, at 760 mm Hg*

Compound	$\Delta d = d$(iso) $- d$ (normal)		$\Delta V = V$(iso) $- V$ (normal)		$\Delta n_D = n_D$(iso) $- n_D$ (normal)		$\Delta R_D = R_D$(iso) $- R_D$ (normal)		$\Delta BP = BP$(iso) $- BP$ (normal)	
	Experimental	Calculated[d]	Experimental	Calculated[d]	Experimental	Calculated[d]	Experimental	Calculated[d]	Experimental	Calculated[d]
C_5H_{12}[b]	*g/ml*	*g/ml*	*ml/mole*	*ml/mole*			*ml/mole*	*ml/mole*	*°C*	*°C*
n-Pentane	0.0000	0.0000	0.00	0.00	0.0000	0.0000	0.000	0.000	0.00	0.0
2-Methylbutane	−.0066	−.0059	1.23	1.09	−.0037	−.0032	.031	.033	−8.30	−8.4
C_6H_{14}										
n-Hexane	0.0000	0.0000	0.00	0.00	0.0000	0.0000	0.000	0.000	0.00	0.0
2-Methylpentane	−.0063	−.0055	1.26	1.09	−.0036	−.0030	.028	.033	−8.49	−8.4
3-Methylpentane	.0049	.0037	−0.96	−0.73	.0015	.0009	−.116	−.104	−5.49	−7.2
2,3-Dimethylbutane	−.0103	−.0093	2.07	1.86	−.0062	−.0052	.024	.049	−19.01	−18.8
2,2-Dimethylbutane	.0022	.0020	−0.43	−0.40	.0000	.0001	−.100	−.085	−10.74	−10.9
C_7H_{16}										
n-Heptane	0.0000	0.0000	0.00	0.00	0.0000	0.0000	0.000	0.000	0.00	0.0
2-Methylhexane	−.0049	−.0050	1.06	1.09	−.0028	−.0028	.025	.033	−8.37	−8.4
3-Methylhexane	.0033	.0034	−0.70	−0.73	.0010	.0009	−.088	−.104	−6.47	−7.2
3-Ethylpentane	.0145	.0121	−3.04	−2.55	.0057	.0046	−.278	−.241	−4.97	−6.0
2,2-Dimethylpentane	−.0099	−.0086	2.15	1.86	−.0054	−.0048	.072	.049	−19.20	−18.8
2,3-Dimethylpentane	.0115	.0105	−2.42	−2.22	.0043	.0039	−.238	−.222	−8.67	−9.7
2,4-Dimethylpentane	−.0109	−.0100	2.37	2.18	−.0061	−.0056	.067	.066	−17.87	−16.8
3,3-Dimethylpentane	.0095	.0089	−2.01	−1.88	.0032	.0030	−.225	−.210	−12.36	−13.0
2,2,3-Trimethylbutane	.0063	.0065	−1.34	−1.38	.0018	.0020	−.175	−.166	−17.54	−17.1
C_8H_{18}[c]										
n-Octane	0.0000	0.0000	0.00	0.00	0.0000	0.0000	0.000	0.000	0.00	0.0
2-Methylheptane	−.0047	−.0047	1.09	1.09	−.0025	−.0026	.045	.033	−8.02	−8.4
3-Methylheptane	.0032	.0032	−0.74	−0.73	.0010	.0008	−.090	−.104	−6.74	−7.2
4-Methylheptane	.0030	.0032	−.46	−0.73	.0004	.0008	−.075	−.104	−7.95	−7.2
3-Ethylhexane	.0109	.0112	−2.48	−2.55	.0041	.0044	−.246	−.241	−7.13	−6.0
2,3-Dimethylhexane	−.0073	−.0079	1.71	1.86	−.0040	−.0045	.058	.049	−18.82	−18.8
2,5-Dimethylhexane	.0107	.0097	−2.44	−2.22	.0040	.0036	−.243	−.222	−10.06	−9.7
2,4-Dimethylhexane	−.0023	−.0016	0.53	0.36	−.0022	−.0018	−.064	−.071	−16.23	−15.6
2,5-Dimethylhexane	−.0091	−.0093	2.13	2.18	−.0050	−.0052	.073	.066	−16.56	−16.8
3,3-Dimethylhexane	.0074	.0082	−1.69	−1.88	.0026	.0028	−.183	−.210	−13.69	−13.0
3,4-Dimethylhexane	.0167	.0179	−3.77	−4.04	.0066	.0072	−.348	−.359	−7.94	−8.5
3-Methyl-3-ethylpentane	.0167	.0179	−3.77	−4.04	.0065	.0072	−.357	−.359	−10.01	−8.5
3-Methyl-3-ethylpentane	.0248	.0252	−5.54	−5.62	.0103	.0106	−.471	−.469	−7.40	−7.2
2,2,3-Trimethylpentane	.0135	.0141	−3.06	−3.20	.0053	.0055	−.286	−.303	−15.82	−15.9
2,2,4-Trimethylpentane	−.0107	−.0125	2.51	2.95	−.0061	−.0071	.065	.082	−26.43	−27.2
2,3,3-Trimethylpentane	.0236	.0228	−5.28	−5.12	.0100	.0096	−.432	−.425	−10.90	−11.3
2,3,4-Trimethylpentane	.0165	.0164	−3.73	−3.71	.0068	.0065	−.321	−.340	−12.19	−12.2

[a] See eq 22.
[b] 2,2-Dimethylpropane (neopentane) not included.
[c] 2,2,3,3-Tetramethylbutane not included.
[d] See eq 43 and table 4.

The final equations, with the standard deviations of a single value, are

$$\Delta V^{20} = -0.6z_3 - 0.8z_4 \pm 2.3 \tag{23}$$

$$\Delta R_D{}^{20} = -0.08z_3 - 0.12z_4 \pm 0.15 \tag{24}$$

$$\Delta BP_{760} = -5.8z_3 - 13.8z_4 \pm 3.9. \tag{25}$$

The units of ΔV^{20} and $\Delta R_D{}^{20}$ are milliliters per mole, and ΔBP_{760} is in degrees centigrade.

The root-mean-square values of ΔV^{20}, $\Delta R_D{}^{20}$, and ΔBP_{760} for the 29 paraffins are ± 2.51, ± 0.211, and ± 12.9, as compared with the

standard deviations from eq 23, 24, and 25, of ± 2.3, ± 0.15, and ± 3.9, respectively. Thus, for the molal volume and molal refraction the standard deviations are not much smaller than the root mean square values of ΔV^{20} and ΔR_D^{20}, so that eq 20 gives a poor representation of the data. For the boiling point the standard deviation is considerably smaller than the root-mean-square value of ΔBP_{760}. However, for all three properties a pronounced improvement in the representation of the data may be effected by allowing for interactions between the CH_3, CH_2, CH, and C groups, as will be shown in the following paragraphs.

The component parts of the paraffin molecule will be taken, as before, as the CH_3, CH_2, CH, and C groups. The number of each group in the ith paraffin hydrocarbon will be z_{1i}, z_{2i}, z_{3i}, and z_{4i}, and their contributions to the property G will be a_1, a_2, a_3, and a_4, respectively. Interactions between adjacent groups only will be considered. Then the possible interactions correspond to the 10 ways in which 2 adjacent groups may occur, CH_3·CH_3, CH_3·CH_2, CH_3·CH, CH_3·C, CH_2·CH_2, . . . , C·C. The number of each interaction in the ith paraffin will be written as z_{11i}, z_{12i}, z_{13i}, z_{14i}, z_{22i}, z_{23i}, z_{24i}, z_{33i}, z_{34i}, and z_{44i}, and their contributions to the property G as a_{11}, a_{12}, a_{13}, a_{14}, a_{22}, a_{23}, a_{24}, a_{33}, a_{34}, and a_{44}, respectively.

Then the value of the property G for the ith paraffin is

$$G_i=\sum_r z_{ri}a_r+\sum_{r,s} z_{rsi}a_{rs}, \tag{26}$$

where the first summation is over the 4 groups, and the second is over the 10 interactions.[6]

In addition to eq 16, and 17 relating to the z_{ri}'s and n_i, the total number of carbon atoms, there exist the following four relations between the z_{ri}'s and the z_{rsi}'s:

$$z_{1i}=2z_{11i}+z_{12i}+z_{13i}+z_{14i} \tag{27}$$

$$2z_{2i}=z_{12i}+2z_{22i}+z_{23i}+z_{24i} \tag{28}$$

$$3z_{3i}=z_{13i}+z_{23i}+2z_{33i}+z_{34i} \tag{29}$$

$$4z_{4i}=z_{14i}+z_{24i}+z_{34i}+2z_{44i}. \tag{30}$$

For the normal paraffins (except ethane and propane) the nonzero z's are z_1, z_2, z_{12}, and z_{22}. It is convenient to eliminate these, and also z_{13}, and z_{14}, by means of eq 16, 17, and eq 27 to 30. Then eq 26 becomes

$$G_i=b_0+n_ib+z_{3i}b_3+z_{4i}b_4+z_{11i}b_{11}+z_{23i}b_{23}+z_{24i}b_{24}+z_{33i}b_{33}+z_{34i}b_{34}+z_{44i}b_{44} \tag{31}$$

where the new constants, the b's, are related to the a's by the equations

$$b_0=2a_1-2a_2+2a_{12}-3a_{22} \tag{32}$$

$$b=a_2+a_{22} \tag{33}$$

$$b_3=a_1-2a_2+a_3-2a_{12}+3a_{13}-a_{23} \tag{34}$$

[6] This is the scheme used by M. L. Huggins [5]. To simplify the problem, Huggins assumed that $a_{11}=a_1$, $a_{14}=a_{23}$, and $a_{24}=a_{33}$. In the present treatment, none of the constants have been eliminated in this manner. Huggins determined the remaining constants by means of the increment (normal to iso-) for selected homologous series. The least squares treatment used here has the advantage that all the available data is utilized uniformly in fixing the constants.

$$b_4 = 2a_1 - 3a_2 + a_4 - 2a_{12} + 4a_{14} - 2a_{22} \quad (35)$$

$$b_{11} = a_{11} - 2a_{12} + a_{22} \quad (36)$$

$$b_{23} = a_{12} - a_{13} - a_{22} + a_{23} \quad (37)$$

$$b_{24} = a_{12} - a_{14} - a_{22} + a_{24} \quad (38)$$

$$b_{33} = 2a_{12} - 2a_{13} - a_{22} + a_{33} \quad (39)$$

$$b_{34} = 2a_{12} - a_{13} - a_{14} - a_{22} + a_{34} \quad (40)$$

$$b_{44} = 2a_{12} - 2a_{14} - a_{22} + a_{44}. \quad (41)$$

All the members of a homologous series, except the first, have the same set of values for the z's in eq 31. This is in qualitative agreement with the anomalous behavior actually observed for the first members of such series. For the remaining members of a homologous series, eq 31 predicts a linear variation of the property G with n, with a constant increment per CH_2 group of b, the same for all series. In particular, for the normal series all the z's in eq 31 vanish, and

$$G_n = b_0 + n_n b. \quad (42)$$

From the present viewpoint, ethane (not methane) is the first member of the normal series, and is anomalous, with $G = b_0 + 2b + b_{11}$. If methane were included in the present scheme, it would be assigned a single and distinct constant, say a_0.

By subtraction of eq 42 from eq 31, the difference in value of the property G between the branched chain paraffin and its normal isomer ($n_i = n_n$) is obtained:

$$\Delta G_i = (G_i - G_n) = z_{3i}b_3 + z_{4i}b_4 + z_{11i}b_{11} + z_{23i}b_{23} + z_{24i}b_{24} + z_{33i}b_{33} + z_{34i}b_{34} + z_{44i}b_{44}. \quad (43)$$

The term $z_{11i}\, b_{11}$ vanishes for all the paraffins except ethane.

As an illustration of eq 43, consider the 2,3-dimethyl series:

Member	Compound	ΔG
First	2,3-Dimethylbutane	$2b_3 + b_{23}$.
Second	2,3-Dimethylpentane	$2b_3 + b_{23} + b_{33}$.
Third	2,3-Dimethylhexane	$2b_3 + b_{23} + b_{33}$.
...	...	...

The values of the z's in eq 43 are given in table 3 for each of the 70 paraffin hydrocarbons, C_5 to C_9.

TABLE 3.—*Values of the z's in equation 43 for each of the 70 paraffins,* C_5 *to* C_9

Compound	z_3	z_4	z_{23}	z_{24}	z_{33}	z_{34}	z_{44}
C_5H_{12}							
n-Pentane	0	0	0	0	0	0	0
2-Methylbutane	1	0	1	0	0	0	0
2,2-Dimethylpropane	0	1	0	0	0	0	0
C_6H_{14}							
n-Hexane	0	0	0	0	0	0	0
2-Methylpentane	1	0	1	0	0	0	0
3-Methylpentane	1	0	2	0	0	0	0
2,2-Dimethylbutane	0	1	0	1	0	0	0
2,3-Dimethylbutane	2	0	0	0	1	0	0

TABLE 3.—*Values of the z's in equation 43 for each of the 70 paraffins,* C_7 *to* C_9—Continued.

Compound	z_3	z_4	z_{23}	z_{24}	z_{33}	z_{34}	z_{44}
C_7H_{16}							
n-Heptane	0	0	0	0	0	0	0
2-Methylhexane	1	0	1	0	0	0	0
3-Methylhexane	1	0	2	0	0	0	0
3-Ethylpentane	1	0	3	0	0	0	0
2,3-Dimethylpentane	0	1	0	1	0	0	0
2,3-Dimethylpentane	2	0	1	0	1	0	0
2,4-Dimethylpentane	2	0	2	0	0	0	0
3,3-Dimethylpentane	0	1	0	2	0	0	0
2,2,3-Trimethylbutane	1	1	0	0	0	1	0
C_8H_{18}							
n-Octane	0	0	0	0	0	0	0
2-Methylheptane	1	0	1	0	0	0	0
3-Methylheptane	1	0	2	0	0	0	0
4-Methylheptane	1	0	2	0	0	0	0
3-Ethylhexane	1	0	3	0	0	0	0
2,2-Dimethylhexane	0	1	0	1	0	0	0
2,3-Dimethylhexane	2	0	1	0	1	0	0
2,4-Dimethylhexane	2	0	3	0	0	0	0
2,5-Dimethylhexane	2	0	2	0	0	0	0
3,3-Dimethylhexane	0	1	0	2	0	0	0
3,4-Dimethylhexane	2	0	2	0	1	0	0
2-Methyl-3-ethylpentane	2	0	2	0	1	0	0
3-Methyl-3-ethylpentane	0	1	0	3	0	0	0
2,2,3-Trimethylpentane	1	1	1	0	0	1	0
2,2,4-Trimethylpentane	1	1	1	1	0	0	0
2,3,3-Trimethylpentane	1	1	0	1	0	1	0
2,3,4-Trimethylpentane	3	0	0	0	2	0	0
2,2,3,3-Tetramethylbutane	0	2	0	0	0	0	1
C_9H_{20}							
n-Nonane	0	0	0	0	0	0	0
2-Methyloctane	1	0	1	0	0	0	0
3-Methyloctane	1	0	2	0	0	0	0
4-Methyloctane	1	0	2	0	0	0	0
3-Ethylheptane	1	0	3	0	0	0	0
4-Ethylheptane	1	0	3	0	0	0	0
2,2-Dimethylheptane	0	1	0	1	0	0	0
2,3-Dimethylheptane	2	0	1	0	1	0	0
2,4-Dimethylheptane	2	0	3	0	0	0	0
2,5-Dimethylheptane	2	0	3	0	0	0	0
2,6-Dimethylheptane	2	0	2	0	0	0	0
3,3-Dimethylheptane	0	1	0	2	0	0	0
3,4-Dimethylheptane	2	0	2	0	1	0	0
3,5-Dimethylheptane	2	0	4	0	0	0	0
4,4-Dimethylheptane	0	1	0	2	0	0	0
2-Methyl-3-ethylhexane	2	0	2	0	1	0	0
2-Methyl-4-ethylhexane	2	0	4	0	0	0	0
3-Methyl-3-ethylhexane	0	1	0	3	0	0	0
3-Methyl-4-ethylhexane	2	0	3	0	1	0	0
2,2,3-Trimethylhexane	1	1	1	0	0	1	0
2,2,4-Trimethylhexane	1	1	2	1	0	0	0
2,2,5-Trimethylhexane	1	1	1	1	0	0	0
2,3,3-Trimethylhexane	1	1	0	1	0	1	0
2,3,4-Trimethylhexane	3	0	1	0	2	0	0
2,3,5-Trimethylhexane	3	0	2	0	1	0	0
2,4,4-Trimethylhexane	1	1	1	2	0	0	0
3,3,4-Trimethylhexane	1	1	1	1	0	1	0
3,3-Diethylpentane	0	1	0	4	0	0	0
2,2-Dimethyl-3-ethylpentane	1	1	2	0	0	1	0
2,3-Dimethyl-3-ethylpentane	1	1	0	2	0	1	0
2,4-Dimethyl-3-ethylpentane	3	0	1	0	2	0	0
2,2,3,3-Tetramethylpentane	0	2	0	1	0	0	1
2,2,3,4-Tetramethylpentane	2	1	0	0	1	1	0
2,2,4,4-Tetramethylpentane	0	2	0	2	0	0	0
2,3,3,4-Tetramethylpentane	2	1	0	0	0	2	0

Equation 43 has been fitted by least squares (see also section II) to the same data as described above for ΔV^{20}; ΔR_D^{20}, and ΔBP_{760} for the same 29 branched paraffins, C_5 to C_8.

The boiling point is not an additive property in the same sense as are the molal volume and the molal refraction. However the degree of correlation of the boiling point is justification for treating it as such. It should be noted that even though G is not strictly linear in n for a normal and a branched homologous series, ΔG is only slightly affected if the departure from linearity is approximately the same for the two series. Actually ΔBP_{760} for a homologous series shows a slow decrease with increasing n, but this has been disregarded here because of the small range of n involved. ΔV and ΔR especially the latter, are nearly constant for a homologous series. The values of the constants b obtained for the paraffin hydrocarbons are shown in table 4. Since the compound 2,2,3,3-tetramethylbutane was not included in the correlation, the value of b_{44} does not appear in the table. The constants given in table 4 may be used with eq 43 to calculate the difference in molal volume (to give density), molal refraction (to give the refractive index), and normal boiling point, between a normal paraffin hydrocarbon and its isomers.

TABLE 4.—*Values of the constants to be used in calculating the difference in mola volume, ΔV^{20}, in molal refraction,[a] ΔR_D^{20}, and in normal boiling point, ΔBP_{760}, between a normal paraffin and a given isomer (see eq 43)*

Constant	For ΔV^{20}	For ΔR_D^{20} [a]	For ΔBP_{760}
	ml/mole	*ml/mole*	*°C*
b_3	2.91	0.170	−9.6
b_4	5.60	.308	−24.6
b_{23}	−1.82	−.137	1.2
b_{24}	−3.74	−.259	5.8
b_{33}	−6.22	−.425	8.3
b_{34}	−9.89	−.644	17.1
b_{44}			

[a] See eq 22.

The manner in which the 6 constants reproduce, by difference from the corresponding normal paraffin, the data on isopentane, 4 isohexanes, 8 isoheptanes, and 16 isooctanes, is shown in table 2, in which the calculated and experimental values are compared, and is summarized in table 5, which gives the average deviation, the maximum deviation, and the standard deviation, for the molal volume, density, molal refraction, refractive index, and boiling point.

TABLE 5.—*Reproducibility of the selected "best" values of molal volume, density, molal refraction,[a] refractive index, and boiling point, for 29 isoparaffins, C_5 to C_8, by means of 6 constants evaluated from the selected values (see eq 43)*

Deviation	Molal volume at 20° C	Density at 20° C	Molal refraction at 20° C	Refractive index at 20° C	Boiling point at 760 mm
	ml/mole	*g/ml*	*ml/mole*	n_D	*°C*
Average	±0.16	±0.00074	±0.013	±0.00042	±0.55
Maximum	.49	.0024	.037	.0011	1.71
Standard (of a single value)	±.20	±.00093	±.016	±.00050	±0.70

[a] See eq 22.

The values of the constants given in table 4 were then used to calculate values of refractive index, density, and boiling point for 33 isononanes (all the branched-chain nonanes except 2,2,3,3-tetramethylpentane which has 2 adjacent neopentyl groups. These values, expressed as the difference between the value for a given isononane and normal nonane, are given in table 6. For 11 of these isonanes, there were available accurate experimental data on refractive index, density, and boiling point. For these 11 nonanes, the differences between the calculated and experimental values of density, refractive index, and boiling point, using the 6 constants evaluated from the data on the paraffins C_5 to C_8 (see text and tables 4 and 5) are summarized in table 7.

TABLE 6.—*Calculated values of the difference, between each of 33 isononanes*[a] *and normal nonane, of the density, d, at 20° C, the refractive index, n_D, at 20° C, and the boiling point, BP, at 760* Hg *(see eq 43 and table 4)*

Compound	$\Delta d = d$ (iso) − d (normal)	$\Delta n_D = n_D$ (iso) − n_D (normal)	$\Delta BP = BP$(iso) − BP (normal)
	g/ml		°C
n-Nonane	0.0000	0.0000	0.0
2-Methyloctane	−.0043	−.0024	−5.4
3-Methyloctane	.0029	.0008	−7.2
4-Methyloctane	.0029	.0008	−7.2
3-Ethylheptane	.0104	.0041	−6.0
4-Ethylheptane	.0104	.0041	−6.0
2,2-Dimethylheptane	−.0074	−.0042	−18.8
2,3-Dimethylheptane	.0090	.0034	−9.7
2,4-Dimethylheptane	−.0014	−.0017	−13.6
2,5-Dimethylheptane	−.0014	−.0017	−15.6
2,6-Dimethylheptane	−.0086	−.0049	−16.8
3,3-Dimethylheptane	.0076	.0027	−13.0
3,4-Dimethylheptane	.0166	.0068	−8.5
3,5-Dimethylheptane	.0039	.0016	−14.4
4,4-Dimethylheptane	.0076	.0027	−13.0
2-Methyl-3-ethylhexane	.0166	.0068	−8.5
2-Methyl-4-ethylhexane	.0039	.0016	−14.4
3-Methyl-3-ethylhexane	.0233	.0099	−7.3
3-Methyl-4-ethylhexane	.0243	.0102	−7.3
2,2,3-Trimethylhexane	.0131	.0051	−15.9
2,2,4-Trimethylhexane	−.0045	−.0035	−26.0
2,2,5-Trimethylhexane	−.0117	−.0066	−27.2
2,3,3-Trimethylhexane	.0212	.0090	−11.8
2,3,4-Trimethylhexane	0229	.0095	−11.0
2,3,5-Trimethylhexane	.0046	.0009	−18.1
2,4,4-Trimethylhexane	.0032	.0002	−21.4
3,3,4-Trimethylhexane	.0290	.0125	−10.1
3,3-Diethylpentane	.0397	.0175	−1.4
2,2-Dimethyl-3-ethylpentane	.0208	.0086	−14.7
2,3-Dimethyl-3-ethylpentane	.0375	.0165	−8.5
2,4-Dimethyl-3-ethylpentane	.0229	.0095	−11.0
2,2,3,4-Tetramethylpentane	.0194	.0079	−18.4
[b] 2,2,4,4-Tetramethylpentane	−.0146	−.0084	−37.6
2,3,3,4-Tetramethylpentane	.0352	.0156	−9.6

[a] 2,2,3,3-Tetramethylpentane not included.
[b] See section V.

TABLE 7.—*Differences between calculated and experimental values of density, refractive index, and boiling point, for 11 branched-chain nonanes for which accurate experimental data were available (see eq 43)*

Deviation	Density at 20° C	Refractive index at 20° C	Boiling point at 760 mm
	g/ml	n_D	°C
Average	±0.0015	±0.0008	±1.2
Maximum	.0038	.0022	3.1
Standard (of a single value)	±.0018	±.0010	±1.5

The constants given in table 4 may be used with eq 43 to calculate by difference from the corresponding normal isomer, values of refractive index, density, and boiling point for the higher paraffins (including decanes, undecanes, dodecanes, etc.), except those having two neopentyl groups once (adjacent) or twice removed from each other. The values of density and refractive index would apply, of course, to the *liquid* state at 20° C. (However, in calculating boiling points, allowance should be made for the slow decrease of ΔBP_{760} for a homologous series with increasing number of carbon atoms.)

After the values of the constants, the b's, have been obtained by the correlation of the data (b_0 and b may be obtained from the limiting linear relation approached by the normal series), it is of considerable interest to inquire how much information may be obtained concerning the original constants characterizing the component parts and interactions of the molecule, the a's. It should be remembered that the b's are to some extent arbitrary, since they depend upon which r's are eliminated from eq 26. This latitude does not, of course, affect the correlation of the data or the values calculated from the constants. However, from a fundamental viewpoint, the a's are more simply defined and of more interest than the b's.

First, it is clear that eq 32 to 35 may be solved for a_1, a_2, a_3, and a_4, provided the a_{rs}'s (interactions) are known. For the determination of the 10 a_{rs}'s there are available only six equations, 36 to 41. Actually, in the present case, only four equations, 37 to 40, are available for the determination of 8 a_{rs}'s, since b_{11} and b_{44} were not determined. Therefore, it is not possible to determine the a_{rs}'s without the introduction of some additional conditions. The reasonable assumption that will be made is that a_{rs} is a simple function of the indices r and s, so that it may be represented by a few terms of a power series (symmetrical) in r and s:[7]

$$a_{rs}=(h_0+h_1r+h_2r^2+\ \ldots\ )+(h_0+h_1s+h_2s^2+\ \ldots\ )+ [k_1(rs)+k_2(r^2s+rs^2)+\ \ldots\ ]. \quad (44)$$

Furthermore, only the cross-terms between r and s need be retained, since the terms in powers of r alone and s alone, may always be assigned to a_r and a_s, respectively (that is, only the cross-terms represent true "interactions"). Therefore, a_{rs} may be written

$$a_{rs}=k_1(rs)+k_2(r^2s+rs^2)+\ \ldots \quad (45)$$

On substitution of eq 45 into eq 36 to 41, there are obtained the following set of equations for the determination of k_1, k_2, . . . (it may be remarked that the terms in eq 44 in r alone, and s alone, would vanish in this substitution):

$$b_{11}=k_1\ +6k_2\ +\ \ldots \quad (46)$$
$$b_{22}=k_1\ +8k_2\ +\ \ldots \quad (47)$$
$$b_{24}=2k_1+18k_2+\ \ldots \quad (48)$$
$$b_{33}=3k_1+26k_2+\ \ldots \quad (49)$$
$$b_{34}=5k_1+48k_2+\ \ldots \quad (50)$$
$$b_{44}=8k_1+84k_2+\ \ldots \quad (51)$$

[7] However, it should be recognized that the assignment of the indices 1, 2, 3, and 4 to the CH_3, CH_2, CH, and C groups is arbitrary. Any linear transformation of the indices, of the form $r'=\alpha+\beta r$, $s'=\alpha+\beta s$ yields an equally valid set of indices. If a_{rs} is expanded in a power series in the generalized indices, r' and s', and r' and s' are then replaced by $(\alpha+\beta r)$ and $(\alpha+\beta s)$, powers series of the same form as eq 44 and 45, are obtained, but h_0, h_1, h_2, . . . , and k_1, k_2, . . . , become functions of α and β. However, it is obvious that the values of the numerical coefficients in eq 46 to 51, which are the essential result of the present discussion, are unchanged.

It has been found that when the b's from table 4, for ΔV^{20}, ΔR_D^{20}, and ΔBP_{760} are substituted in eq 47 to 50, these four equations are approximately satisfied when only the first constant k_1, is retained. Very little improvement is effected by retaining also k_2. Thus, if only k_1 is retained, the least-squares value of k_1 is

$$k_1=\left(\frac{b_{23}+2b_{24}+3b_{33}+5b_{34}}{1^2+2^2+3^2+5^2}\right), \tag{52}$$

and the calculated values are

Property	Value of k_1
ΔV^{20}	−1.98 ml/mole.
ΔR_D^{20}	−0.132 ml/mole
ΔBP_{760}	2.2° C

The values of the b's calculated from these values of k_1 are compared with the observed values in table 8. The agreement is not as good for ΔBP_{760} as for ΔV^{20} and ΔR_D^{20}.

TABLE 8.—*Comparison of the observed values of the constants (b's) and the values calculated from the first term of equations 46 to 51*

Constant	ΔV^{20}		ΔR_D^{20} *		ΔBP_{760}	
	Observed	Calculated	Observed	Calculated	Observed	Calculated
	ml/mole	*ml/mole*	*ml/mole*	*ml/mole*	*°C*	*°C*
b_{11}		−1.98		−0.132		3.1
b_{23}	−1.82	−1.98	−0.137	−.132	1.2	1.5
b_{24}	−3.74	−3.96	−.259	−.264	5.8	6.2
b_{33}	−6.22	−5.94	−.425	−.396	8.3	9.4
b_{34}	−9.89	−9.90	−.644	−.660	17.1	15.8
b_{44}		−15.84		−1.056		23.2

* See eq 22.

IV. APPLICATION TO MONOOLEFIN HYDROCARBONS

In applying the present method to the monoolefins, the quantity correlated was the value of the given property for a given monoolefin less the value for the parent paraffin. This difference will be denoted by ΔG. The parent paraffin hydrocarbon is defined as the paraffin with the same carbon skeleton as the olefin; in other words, replacement of the double bond in an olefin by a single bond yields the parent paraffin hydrocarbon. Obviously several olefins may have the same parent paraffin.

This approach is useful because the data on the paraffin hydrocarbons are more complete and more accurate than the data on the monoolefins. Thus the data on the octanes, which are now complete, provide the basis for the calculation of the properties of the octenes, for many of which the data are missing or quite inaccurate.

In the correlation of the paraffin hydrocarbons the Lorentz molal refraction, defined by eq 22, was used. Because of the labor involved in calculating the Lorentz refraction, it was decided in the case of the monoolefins to use the Gladstone-Dale type of molal refraction,

$$R_D^{20}=\frac{M}{d^{20}}(n_D^{20}-1), \tag{53}$$

which was used by Huggins [5, 6]. It is probable that in either case the correlation leads to essentially the same calculated refractive indices.

The correlation of the increment of the molal volume at 20° C, ΔV^{20}, the increment of the molal refraction for the *D* line at 20° C, ΔR_D^{20}, and the increment of the boiling point at 760 mm, ΔBP_{760}, has been carried out for 58 monoolefins, C_5 to C_7 (the only compound of the 59 in the C_5 to C_7 range omitted was 3,4-dimethyl-1-pentene, for which no data were available to the authors).

The values of these properties for the monoolefins, and for the parent paraffin hydrocarbons (C_5 to C_7), were taken from the tables of the American Petroleum Institute Research Project 44 as of September 30, 1943.

These data, expressed as the difference between the values for a given monoolefin and the corresponding paraffin with the same carbon skeleton, are given in table 9.

The simplest scheme for the correlation of ΔG would be the assignment of a single constant for the contribution of the double bond. The least squares value of the constant is then the average value of ΔG for the 58 monoolefins. The average value of ΔV^{20}, ΔR_D^{20}, and ΔBP_{760} are shown in table 10, together with the maximum deviation of a single value, and the standard deviation (of a single value).

In order to improve the representation of the data, the double bonds may be divided into classes in a suitable way, and a constant assigned to each class. The classification chosen here depends on the number and location of the attached alkyl groups (indicated by R), as shown below:[8]

Type I	$H_2C=CHR$
Type II	$RHC=CHR$
Type III	$H_2C=CR_2$
Type IV	$RHC=CR_2$
Type V	$R_2C=CR_2$

In each type except type *I* it is possible for geometrical (*cis-* and *trans-*) isomers to occur, with comparatively small differences in physical properties. In all the present calculations geometrical isomers were treated as distinct compounds (of the same class), so that the constants derived refer to an average value for *cis-* and *trans-*isomers. The same result would be obtained by averaging the properties of the two isomers and then giving it a weight of two in the calculations. The decision not to distinguish *cis-* and *trans-*isomers in the calculations was made because the *cis-trans* difference does not appear to be very regular, and is, for all except a few compounds, of the same order as the uncertainty of the experimental data.

The average values of ΔV^{20}, ΔR_D^{20}, and ΔBP_{760} for each of the five

[8] See reference [5] and the references given therein.

TABLE 9.—*Experimental and calculated values of the difference, between each of 58 monoolefins, C_5 to C_7, and the corresponding paraffin having the same carbon skeleton, of the density d, at 20° C, the molal volume, V, at 20° C, the refractive index, n_D, at 20° C, the molal refraction, [a] R_D, at 20° C, and the boiling point, BP, at 760 mm Hg*

Compound	Type	Δd^{20}		ΔV^{20}		Δn_D^{20}		ΔR_D^{20} [a]		ΔBP_{760}	
		Experimental	Calculated [b]	Experimental	Calculated [b]	Experimental	Calculated [b]	Experimental	Calculated [b]	Experimental	Calculated [b]
C_5H_{10}		*g/ml*	*g/ml*	*ml/mole*	*ml/mole*			*ml/mole*	*ml/mole*	*° C*	*° C*
1-Pentene	I	0.0153	0.0131	−5.89	−5.52	0.0135	0.0129	−0.63	−0.56	−5.98	−5.06
cis-2-Pentene	II	.0298	.0256	−8.30	−7.61	.0245	.0221	−.35	−.35	0.92	0.00
trans-2-Pentene	II	.0228	.0256	−7.15	−7.61	.0220	.0221	−.18	−.35	−.08	.00
2-Methyl-1-butene	III	.0307	.0284	−8.59	−8.21	.0240	.0220	−1.17	−.53	3.24	1.92
3-Methyl-1-butene	I	.0075	.0054	−4.56	−4.18	.0106	.0106	−0.34	−.72	−7.71	−9.02
2-Methyl-2-butene	IV	.0425	0359	−10.52	−9.45	.0336	.0283	−.16	−.32	10.54	5.63
C_6H_{12}											
1-Hexene	I	0.0156	0.0130	−6.00	−5.52	0.0131	0.0120	−0.61	−0.56	−5.24	−5.06
cis-2-Hexene	II	.0246	.0244	−7.64	−7.61	.0206	.0203	−.33	−.35	−0.14	0.00
trans-2-Hexene	II	.0196	.0244	−6.74	−7.61	.0186	.0203	−.22	−.35	−.74	.00
cis-3-Hexene	II	.0196	.0186	−6.74	−6.56	.0186	.0183	−.22	−.19	−1.34	−1.60
trans-3-Hexene	II	.0186	.0186	−6.56	−6.56	.0191	.0183	−.09	−.19	−0.74	−1.60
2-Methyl-1-pentene	III	.0289	.0271	−8.54	−8.21	.0211	.0203	−.57	−.53	1.93	1.92
3-Methyl-1-pentene	I	.0057	.0061	−4.11	−4.18	.0070	.0068	−.67	−.72	−9.48	−9.02
4-Methyl-1-pentene	I	.0119	.0126	−5.39	−5.52	.0126	.0118	−.40	−.56	−6.27	−5.06
2-Methyl-2-pentene	IV	.0359	.0281	−9.80	−8.40	.0289	.0239	−.11	−.16	6.93	4.03
cis(?)-3-Methyl-2-pentene	IV	.0299	.0294	−8.49	−8.40	.0251	.0248	−.15	−.16	4.52	4.03
trans(?)-3-Methyl-2-pentene	IV	.0343	.0294	−9.26	−8.40	.0280	.0248	−.11	−.16	7.22	4.03
cis(?)-4-Methyl-2-pentene	II	.0189	.0166	−6.71	−6.27	.0176	.0145	−.29	−.51	−4.27	−3.96
trans(?)-4-Methyl-2-pentene	II	.0189	.0166	−6.71	−6.27	.0176	.0145	−.29	−.51	−1.77	−3.96
2-Ethyl-1-butene	III	.0252	.0224	−7.67	−7.16	.0205	.0190	−.39	−.37	1.72	0.32
2,3-Dimethyl-1-butene	III	.0164	.0205	−6.13	−6.87	.0152	.0152	−.41	−.69	−2.37	−2.04
3,3-Dimethyl-1-butene	I	.0037	.0036	−3.84	−3.82	.0072	.0080	−.48	−.38	−8.50	−8.81
2,3-Dimethyl-2-butene	V	.0472	.0426	−11.52	−10.74	.0371	.0346	.09	.11	15.26	12.03
C_7H_{14} [c]											
1-Heptene	I	0.0133	0.0125	−5.69	−5.52	0.0117	0.0112	−0.56	−0.56	−5.13	−5.06
cis-2-Heptene	II	.0243	.0230	−7.87	−7.61	.0183	.0187	−.52	−.35	0.07	0.00
trans-2-Heptene	II	.0203	.0230	−7.09	−7.61	.0183	.0187	−.20	−.35	−.43	.00
cis-3-Heptene	II	.0183	.0177	−6.69	−6.56	.0163	.0168	−.32	−.19	−2.63	−1.60
trans-3-Heptene	II	.0173	.0177	−6.49	−6.56	.0163	.0168	−.24	−.19	−2.63	−1.60
2-Methyl-1-hexene	III	.0212	.0255	−7.35	−8.21	.0191	.0189	−.15	−.53	1.25	1.92
3-Methyl-1-hexene	I	.0080	.0060	−4.58	−4.18	.0083	.0063	−.61	−.72	−7.95	−9.02
4-Methyl-1-hexene	I	.0099	.0127	−4.97	−5.52	.0098	.0112	−.55	−.56	−4.65	−5.06
5-Methyl-1-hexene	I	.0152	.0122	−6.14	−5.52	.0111	.0110	−.50	−.56	−5.50	−5.06
2-Methyl-2-hexene	IV	.0302	.0268	−9.13	−8.40	.0251	.0231	−.04	−.16	4.26	4.03
cis-3-Methyl-2-hexene	IV	.0259	.0273	−7.85	−8.40	.0213	.0230	−.18	−.16	1.53	4.03

2-Methyl-1-hexene	III	.0212	.0255	−7.35	−8.21	.0191	.0189	−.15	−.53	1.25	1.92
3-Methyl-1-hexene	I	.0080	.0060	−4.58	−4.18	.0063	.0063	−.61	−.72	−7.95	−9.02
4-Methyl-1-hexene	I	.0099	.0127	−4.97	−5.52	.0098	.0112	−.55	−.56	−4.65	−5.06
5-Methyl-1-hexene	I	.0152	.0122	−6.14	−5.52	.0111	.0110	−.89	−.56	−4.55	−5.06
2-Methyl-2-hexene	IV	.0303	.0253	−9.13	−8.40	.0251	.0251	−.08	−.16	4.40	4.03
cis-3-Methyl-2-hexene	IV	.0250	.0273	−7.95	−8.40	.0213	.0226	−.15	−.16	1.55	4.03
trans-3-Methyl-2-hexene	IV	.0250	.0273	−7.95	−8.40	.0213	.0226	−.15	−.16	1.55	4.03
cis-4-Methyl-2-hexene	II	.0130	.0164	−5.59	−6.27	.0103	.0138	−.73	−.51	−4.95	−3.96
trans-4-Methyl-2-hexene	II	.0110	.0164	−5.19	−6.27	.0103	.0138	−.57	−.51	−6.45	−3.96
cis-5-Methyl-2-hexene	II	.0212	.0225	−7.35	−7.61	.0151	.0185	−.72	−.35	−0.55	0.00
trans-5-Methyl-2-hexene	II	.0212	.0225	−7.35	−7.61	.0151	.0185	−.72	−.35	−2.55	.00
cis-2-Methyl-3-hexene	II	.0152	.0107	−6.14	−5.22	.0141	.0117	−.37	−.35	−3.05	−5.56
trans-2-Methyl-3-hexene	II	.0152	.0107	−6.14	−5.22	.0141	.0117	−.37	−.35	−3.05	−5.56
cis-3-Methyl-3-hexene	IV	.0160	.0219	−6.19	−7.35	.0183	.0206	.15	.00	2.05	2.43
trans-3-Methyl-3-hexene	IV	.0160	.0219	−6.19	−7.35	.0183	.0206	.15	.00	2.05	2.43
2-Ethyl-1-pentene	III	.0210	.0209	−7.17	−7.16	.0163	.0174	−0.52	−0.37	2.05	0.32
3-Ethyl-1-pentene	I	−.0012	.0065	−2.65	−4.18	.0046	.0066	−.40	−.72	−8.47	−9.02
2,3-Dimethyl-1-pentene	III	.0104	.0201	−4.98	−6.87	.0100	.0146	−.56	−.69	−5.59	−2.04
2,4-Dimethyl-1-pentene	III	.0210	.0250	−7.41	−8.21	.0154	.0185	−.65	−.53	0.49	1.92
3,3-Dimethyl-1-pentene	I	.0032	.0045	−3.56	−3.82	.0075	.0079	−.34	−.38	−9.06	−8.81
4,4-Dimethyl-1-pentene	I	.0111	.0119	−5.35	−5.52	.0097	.0108	−.66	−.56	−6.80	−5.06
3-Ethyl-2-pentene	IV	.0218	.0229	−7.15	−7.35	.0196	.0212	−.14	.00	1.53	2.43
2,3-Dimethyl-2-pentene	V	.0309	.0351	−8.91	−9.69	.0280	.0303	.29	.27	7.21	10.43
2,4-Dimethyl-2-pentene	IV	.0230	.0193	−7.81	−7.06	.0204	.0167	−.10	−.32	1.49	0.07
cis-3,4-Dimethyl-2-pentene	IV	.0174	.0211	−6.35	−7.06	.0130	.0179	−.70	−.32	−3.29	.07
trans-3,4-Dimethyl-2-pentene	IV	.0174	.0211	−6.35	−7.06	.0130	.0179	−.70	−.32	−3.29	.07
cis-4,4-Dimethyl-2-pentene	II	.0141	.0138	−5.97	−5.91	.0163	.0147	.04	−.17	−3.20	−3.75
trans-4,4-Dimethyl-2-pentene	II	.0141	.0138	−5.97	−5.91	.0163	.0147	.04	−.17	−3.20	−3.75
3-Methyl-2-ethyl-1-butene	III	.0234	.0147	−7.52	−5.82	.0200	.0127	−.22	−.53	−0.99	−1.64
2,3,3-Trimethyl-1-butene	III	.0150	.0179	−5.94	−6.51	.0134	.0158	−.45	−.35	−3.01	−1.83

[a] See eq 53.
[b] 3,4-Dimethyl-1-pentene (type I) not included.
[c] See eq 56 and table 12.

TABLE 10.—*Reproducibility of the selected "best" values of molal volume, molal refraction,[a] and boiling point for 58 monoolefins by means of 1 constant (for each property)*

	ΔV^{20}	ΔR_D^{20} [a]	ΔBP_{760}
	ml/mole	*ml/mole*	*°C*
Average value	−6.75	−0.36	−1.24
Maximum deviation	4.77	0.81	11.8
Standard deviation (of a single value)	±1.66	±0.29	±4.85

[a] See eq 53.

classes are shown in table 11. These are the least squares values of the corresponding constants. There is also given the standard deviation (of a single value) for each property, for each type, and also for the entire group. The latter figure represents the error when the 58 olefins are correlated with these 5 constants and should be compared with the standard deviation in table 10 for 1 constant. The improvement is greatest for ΔBP_{760} and least for ΔR_D^{20}.

TABLE 11.—*Reproducibility of the selected "best" values of molal volume, molal refraction,[a] and boiling point for 58 monoolefins by means of 5 constants, 1 for each type (for each property)*

Type	Number of compounds	ΔV^{20}		ΔR_D^{20} [a]		ΔBP_{760}	
		Average value	Deviation	Average value	Deviation	Average value	Deviation
		ml/mole	*ml/mole*	*ml/mole*	*ml/mole*	*°C*	*°C*
I	13	−4.83	±1.02	−0.54	±0.14	−6.91	±1.65
II	20	−6.72	±0.75	−.33	±.22	−2.04	±1.84
III	10	−7.13	±1.08	−.51	±.26	−0.13	±2.64
IV	13	−7.93	±1.42	−.17	±.25	+2.87	±3.75
V	2	−10.22	±1.26	+.19	±.32	+11.24	±4.01
I to V	58		±1.07		±0.22		±2.89

[a] See eq 53.

The five constants introduced above take account only of the number and location of alkyl groups about the double bond. However, as has been pointed out by other workers,[9] the properties of a monoolefin are affected considerably by branching of the alkyl groups. In order to take some account of this effect, without introducing too many complications, it was decided to consider only branching on carbon atoms adjacent to the two doubly bonded carbon atoms. The constants were defined in the following way.

Let z_{Ii}, z_{IIi}, . . . , z_{Vi} be the number of double bonds of types I, II, . . . , V in the ith monoolefin, and let a_I, a_{II}, . . . , a_V be the contributions of each type of bond to ΔG. Obviously, for each monoolefin one of the numbers z_I, z_{II}, . . . , z_V is unity and the remaining four are zero. In spite of this apparently trivial reduction, the formalism is convenient in the least squares solution. In addition, let z_{1i}, z_{2i}, z_{3i}, and z_{4i} be the number of primary, secondary, tertiary, and quarternary carbon atoms, respectively, adjacent to the

[9] See reference [8] and the references given there.

two doubly bonded carbon atoms in the ith monoolefin, and let a_1, a_2, a_3, and a_4 be their contributions to ΔG. Then ΔG_i, for the ith monoolefin may be written

$$\Delta G_i = z_{1i}a_1 + z_{\text{II}i}a_{\text{II}} + z_{\text{III}i}a_{\text{III}} + z_{\text{IV}i}a_{\text{IV}} + z_{\text{V}i}a_{\text{V}} + z_{1i}a_1 + z_{2i}a_2 + z_{3i}a_3 + z_{4i}a_4. \quad (54)$$

It is easily seen that one redundant z has been introduced, which may be eliminated from the relation

$$z_{1i} + z_{2i} + z_{3i} + z_{4i} = z_{1i} + 2z_{\text{II}i} + 2z_{\text{III}i} + 3z_{\text{IV}i} + 4z_{\text{V}i}. \quad (55)$$

If z_{1i} is eliminated, ΔG_i becomes

$$\Delta G_i = z_{1i}b_1 + z_{\text{II}i}b_{\text{II}} + z_{\text{III}i}b_{\text{III}} + z_{\text{IV}i}b_{\text{IV}} + z_{\text{V}i}b_{\text{V}} + z_{2i}b_2 + z_{3i}b_3 + z_{4i}b_4, \quad (56)$$

where the new constants, the b's, are related to the a's by the equations

$$\begin{aligned} b_1 &= a_1 + a_1 \\ b_{\text{II}} &= a_{\text{II}} + 2a_1 \\ b_{\text{III}} &= a_{\text{III}} + 2a_1 \\ b_{\text{IV}} &= a_{\text{IV}} + 3a_1 \\ b_{\text{V}} &= a_{\text{V}} + 4a_1 \\ b_2 &= a_2 - a_1 \\ b_3 &= a_3 - a_1 \\ b_4 &= a_4 - a_1 \end{aligned} \quad (57)$$

The following reductions in the coefficients of the normal equations (see eq 9) facilitate the solution for the least squares values of the constants ($\sum_i$ indicates summation over the entire group of monoolefins, $\sum_{\text{I}}$ over those of type I, etc.

$$\sum_i z_{1i}^2 = \sum_{\text{I}} z_{1i}^2 = \sum_{\text{I}} (1), \text{ etc.}, \quad (58a)$$

$$\sum_i z_{1i}z_{\text{II}i} = 0, \text{ etc.} \quad (58b)$$

That is, the sums in which only one roman subscript occurs are equal to the number of olefins of the corresponding type, whereas the sums in which the roman subscripts are different all vanish. As a result the normal equations are easily reduced to three simultaneous linear equations for b_2, b_3, and b_4, after which b_{I}, b_{II}, . . . , b_{V} are obtained from separate equations.

The values of the b's corresponding to ΔV^{20}, ΔR_D^{20}, and ΔBP_{760}, obtained by fitting eq 56 by least squares (see also section II) to the data on the 58 monoolefins, are given in table 12.

TABLE 12.—*Values of the constants to be used in calculating the difference in molal volume, ΔV^{20}, in molal refraction,[a] ΔR_D^{20}, and in normal boiling point, ΔBP_{760}, between a given monoolefin and the corresponding paraffin hydrocarbon having the same carbon skeleton (see eq 56)*

Constant	For ΔV^{20}	For ΔR_D^{20} [a]	For ΔBP_{760}
	ml/mole	*ml/mole*	*°C*
b_I	−6.57	−0.72	−2.46
b_{II}	−8.66	−.51	+1.60
b_{III}	−9.26	−.69	+3.32
b_{IV}	−9.45	−.32	+5.63
b_V	−10.74	+.11	+12.01
b_1	+1.05	+.16	−1.60
b_2	+2.39	.00	−3.56
b_4	+2.75	+.34	−5.35

[a] See eq 53.

The manner in which eq 56 and the constants of table 12 reproduce, by difference from the corresponding parent paraffin hydrocarbon, the data on 58 monoolefins, is shown in table 9, in which the calculated and experimental values are compared, and is summarized in tables 13 and 14. Table 13 shows, for V^{20}, R_D^{20}, and BP_{760}, the standard deviation (of a single value), for each type of olefin, as well as for the entire group. Table 14 shows, for the entire group of 58 monoolefins, the average deviation, the maximum deviation, and the standard deviation (of a single value) for each of the 5 properties: V^{20}, d^{20}, R_D^{20}, n_D^{20}, and BP_{760}.

TABLE 13.—*Reproducibility of the selected "best" values of molal volume, molal refraction,[a] and boiling point for 58 monoolefins by means of 8 constants (see eq 56)*

Type	Number of compounds	Standard deviation (of a single value)		
		V^{20}	R_D^{20} [a]	BP_{760}
		ml/mole	*ml/mole*	*°C*
I	13	±0.54	±0.16	±0.83
II	20	±0.53	±.18	±1.35
III	10	±1.19	±.28	±1.74
IV	13	±0.84	±.59	±2.50
V	2	±.78	±.02	±3.23
I to V	58	±0.77	0.21	±1.74

[a] See eq 53.

TABLE 14.—*Reproducibility of the selected "best" values of molal volume, density, molal refraction,[a] refractive index, and boiling point for 58 monoolefins by means of 8 constants (see eq 56)*

Deviation	V^{20}	d^{20}	R_D^{20} [a]	n_D^{20}	BP_{760}
	ml/mole	*g/ml*	*ml/mole*		*°C*
Average	±0.56	±0.0031	±0.15	±0.0020	±1.33
Maximum	1.89	.0097	.64	.0073	4.91
Standard (of a single value)	±0.71	±.0038	±0.20	±.0025	±1.74

[a] See eq 53.

Values of ΔV^{20}, ΔR_D^{20}, and ΔBP_{760}, obtained from eq 56 and the constants in table 12, were also calculated for the 66 octenes (*cis*- and *trans*-isomers are not distinguished by the present method of calculation) and these values are given in table 15.

TABLE 15.—*Calculated values of the difference, between each of 60 octenes and the corresponding octane having the same carbon skeleton, of the density, d, at 20° C, the refractive index, n_D, at 20° C, and the boiling point, BP, at 760 mm* Hg (see eq 56 and table 12)

Compound	Type	Δd^{20}	Δn_D^{20}	ΔBP_{760}
		g/ml		*° C*
1-Octene	I	0.0119	0.0103	−5.06
*2-Octene	II	.0215	.0173	0.00
*3-Octene	II	.0166	.0168	−1.60
*4-Octene	II	.0166	.0168	−1.60
2-Methyl-1-heptene	III	.0239	.0175	1.92
3-Methyl-1-heptene	I	.0089	.0089	−2.02
4-Methyl-1-heptene	I	.0120	.0104	−5.06
5-Methyl-1-heptene	I	.0120	.0104	−5.06
6-Methyl-1-heptene	I	.0116	.0102	−5.06
2-Methyl-2-heptene	IV	.0248	.0203	4.03
*3-Methyl-2-heptene	IV	.0255	.0208	4.03
*4-Methyl-2-heptene	II	.0154	.0127	−3.96
*5-Methyl-2-heptene	II	.0217	.0174	0.00
*6-Methyl-2-heptene	II	.0211	.0170	0.00
*2-Methyl-3-heptene	II	.0103	.0108	−5.56
*3-Methyl-3-heptene	IV	.0205	.0189	2.43
*4-Methyl-3-heptene	IV	.0204	.0189	2.43
*5-Methyl-3-heptene	II	.0106	.0110	−5.56
*6-Methyl-3-heptene	II	.0163	.0153	−1.60
2-Ethyl-1-hexene	III	.0196	.0160	0.32
3-Ethyl-1-hexene	I	.0062	.0061	−2.02
4-Ethyl-1-hexene	I	.0124	.0106	−5.06
2,3-Dimethyl-1-hexene	III	.0188	.0135	−2.04
2,4-Dimethyl-1-hexene	III	.0241	.0175	1.92
2,5-Dimethyl-1-hexene	III	.0235	.0172	1.92
3,3-Dimethyl-1-hexene	I	.0044	.0073	−8.81
3,4-Dimethyl-1-hexene	I	.0064	.0062	−2.02
3,5-Dimethyl-1-hexene	I	.0057	.0058	−2.02
4,4-Dimethyl-1-hexene	I	.0122	.0106	−5.06
4,5-Dimethyl-1-hexene	I	.0124	.0106	−5.06
5,5-Dimethyl-1-hexene	I	.0115	.0101	−5.06
*3-Ethyl-2-hexene	IV	.0211	.0193	2.43
*4-Ethyl-2-hexene	II	.0160	.0130	−3.96
2,3-Dimethyl-2-hexene	V	.0326	.0276	10.43
2,4-Dimethyl-2-hexene	IV	0.0188	.0159	0.07
2,5-Dimethyl-2-hexene	IV	.0244	.0201	4.03
*3,4-Dimethyl-2-hexene	IV	.0202	.0167	0.07
*3,5-Dimethyl-2-hexene	IV	.0250	.0204	4.03
*4,4-Dimethyl-2-hexene	II	.0141	.0142	−3.75
*4,5-Dimethyl-2-hexene	II	.0160	.0130	−3.96
*5,5-Dimethyl-2-hexene	II	.0209	.0169	0.00
3-Ethyl-3-hexene	IV	.0161	.0175	0.83
*2,2-Dimethyl-3-hexene	II	.0086	.0119	−5.35
*2,3-Dimethyl-3-hexene	IV	.0148	.0146	−1.53
*2,4-Dimethyl-3-hexene	IV	.0139	.0141	−1.53
*2,5-Dimethyl-3-hexene	II	.0042	.0063	−9.52
*3,4-Dimethyl-3-hexene	V	.0280	.0261	8.83
2-*n*-Propyl-1-pentene	III	.0196	.0160	0.32
2-Isopropyl-1-pentene	III	.0202	.0164	0.32
3-Methyl-2-ethyl-1-pentene	III	.0142	.0119	−3.64
4-Methyl-2-ethyl-1-pentene	III	.0192	.0158	0.32
2-Methyl-3-ethyl-1-pentene	III	.0192	.0138	−2.04
3-Methyl-3-ethyl-1-pentene	I	.0050	.0076	−8.81
4-Methyl-3-ethyl-1-pentene	I	.0064	.0062	−9.02
2,3,3-Trimethyl-1-pentene	III	.0180	.0153	−1.83
2,3,4-Trimethyl-1-pentene	III	.0193	.0137	−2.04
2,4,4-Trimethyl-1-pentene	III	.0233	.0171	1.92
3,3,4-Trimethyl-1-pentene	I	.0049	.0076	−8.81
3,4,4-Trimethyl-1-pentene	I	.0062	.0061	−9.02
2-Methyl-3-ethyl-2-pentene	V	.0280	.0261	8.83
*4-Methyl-3-ethyl-2-pentene	IV	.0151	.0149	−1.53
2,3,4-Trimethyl-2-pentene	V	.0265	.0232	6.47
2,4,4-Trimethyl-2-pentene	IV	.0165	.0167	0.28
*3,4,4-Trimethyl-2-pentene	IV	.0181	.0178	0.28
3-Methyl-2-isopropyl-1-butene	III	.0078	.0073	−7.60
3,3,-Dimethyl-2-ethyl-1-butene	III	.0122	.0130	−3.43

*Cis and *trans* forms.

V. DISCUSSION

It is to be noted that, in the preceding treatments, no account has been taken of interactions between parts of the molecule which are not directly bound, as is the case in the 2,2,4,4-tetramethyl structure. It can be seen from scale models of such molecules that an appreciable amount of interaction may exist between parts of the molecule which are not bound directly. For these and similar structures, therefore, one or more additional constants must be introduced in order to make a reliable calculation of the value of a given property. One way of deducing the existence of significant interactions between groups not directly bound to one another is to note any extreme differences between the actual values of the properties of a given molecule and the values that are calculated on the assumption of no interaction between groups not directly bound to one another.

It may be well to remark that the Lorentz expression for the molal refraction has a theoretical foundation and that it is possible to connect the parameters evaluated in this paper with the optical properties of the valence electrons of the hydrocarbon molecules. The parameters evaluated in connection with the molal volume and boiling point are essentially empirical since these phase properties depend not only on the properties of single molecules but also largely on the interactions between molecules.

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SEPARATION AND DETERMINATION OF AROMATIC AND MONOOLEFIN HYDROCARBONS IN MIXTURES WITH PARAFFINS AND NAPHTHENES BY ADSORPTION[1]

By Beveridge J. Mair

ABSTRACT

A new method is described for separating and determining aromatic and monoolefin hydrocarbons in mixtures with paraffins and naphthenes by adsorption. The mixture to be analysed is introduced into the top of a column of silica gel and, when the liquid level just reaches the top of the silica gel, a suitable desorbing liquid, such as ethyl alcohol, is added. The desorbing liquid forces the hydrocarbon portion down the column, during which passage the hydrocarbon portion is fractionated according to the adsorbability of the various components. These components issue from the bottom of the column in the following order: Paraffin plus naphthene, monoolefin, and aromatic hydrocarbons. The analysis is made by determining the fraction of the total volume constituted by each of these classes.

Results of the analyses of five solutions containing aromatic and paraffin hydrocarbons, and three solutions containing aromatic, monoolefin, and paraffin hydrocarbons are given. A procedure is outlined for determining the aromatic content of a straight-run petroleum distillate, as in the gasoline or kerosine fractions

CONTENTS

	Page
I. Introduction	436
II. General description	436
III. Apparatus and material	436
IV. Method and results	439
1. Aromatic hydrocarbons in mixtures with paraffins and naphthenes	439
(a) Procedure	439
(b) Dimensions of the adsorption column	440
(c) Effect of particle size of the adsorbent	441
(d) Effect of rate of flow	442
(e) Desorbing liquid	442
(f) Experimental results	443
2. Aromatic and monoolefin hydrocarbons in mixtures with paraffins and naphthenes	445
(a) Procedure	445
(b) Behavior of olefins	448
(c) Experimental results	449
V. Recommended procedure for the determination of the aromatic content of a straight-run petroleum distillate	450
VI. References	451

[1] This investigation was performed jointly with the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the "Analysis, Purification, and Properties of Petroleum Hydrocarbons."

I. INTRODUCTION

This report describes a new method for separating and determining aromatic and monoolefin hydrocarbons in mixtures with paraffins and naphthenes by absorption. In comparison with the method previously reported for the determination of aromatic hydrocarbons by adsorption [1]*, the method described here is simpler and more accurate because it involves no calibration of the adsorbents with the hydrocarbons involved.

II. GENERAL DESCRIPTION

This method is a development of the Tswett or chromatographic method of analysis [2, 3]. The sample to be analysed (a mixture of aromatic, monoolefin, and paraffin plus naphthene hydrocarbons) is introduced into a reservoir at the top of a column of silica gel. When the sample has completely entered the adsorbent, an appropriate desorbing liquid, such as ethyl alcohol, is added to the reservoir. The desorbing liquid forces the hydrocarbon portion down the column, during which passage the hydrocarbon portion is fractionated and separated into three contiguous zones according to the adsorbability of the components. The lowest zone contains the naphthenes and paraffins, the middle zone the monoolefins, and the top zone the aromatic hydrocarbons. The liquid issuing from the bottom of the column is collected in appropriate small fractions, with the experiment being terminated as soon as substantially pure desorbing liquid issues. The volumes and refractive indices of the fractions of filtrate are determined, and a plot of the refractive index of the filtrate as a function of its volume is made. From this plot, the volume and percentage by volume of each of the three groups of hydrocarbons, (a) paraffins plus naphthenes, (b) monoolefins, and (c) aromatic hydrocarbons, are determined.

III. APPARATUS AND MATERIAL

An apparatus which may be used for this method of analysis is shown in figure 1. The apparatus, made of Pyrex glass, consists essentially of the reservoir, *E*, sealed to the column proper, which itself consists of a section, *F*, sealed to a section of smaller diameter, *I*. At the bottom of section *I* is sealed a sintered glass plate, *J*, of medium or fine porosity, which serves to retain the silica gel, *G*. Below *J* is stopcock *K* and the ground joint, *L* (standard taper 19/38), through which the graduated receiver *O* is attached. The diameter of the bore of the stopcock plugs, *K* and *P*, is 2 mm. The outside diameter of the outlet, *N*, is 6 mm. *M* is a capillary vent. The volume of the tube between the sintered plate, *J*, and stopcock *K* is 2.0 ml.[2]

It is desirable to have two receivers, one with a capacity of 1.1 ml, graduated to 0.01 ml with 0.001 ml estimated, the other with a capacity of 11 ml, graduated to 0.1 ml with 0.01 ml estimated. To

*Figures in brackets indicate the literature references at the end of this paper.

[2] When stopcock *K* is closed for the measurement and withdrawal of a fraction, liquid and noncondensible gas collects in this space and the pressure produced may cause leakage of the stopcock if this space is too small. On the other hand, this space should not be too large, as this increases the hold-up. It is necessary also that the plug of the stopcock be held firmly in its shell with spring clamps or other device.

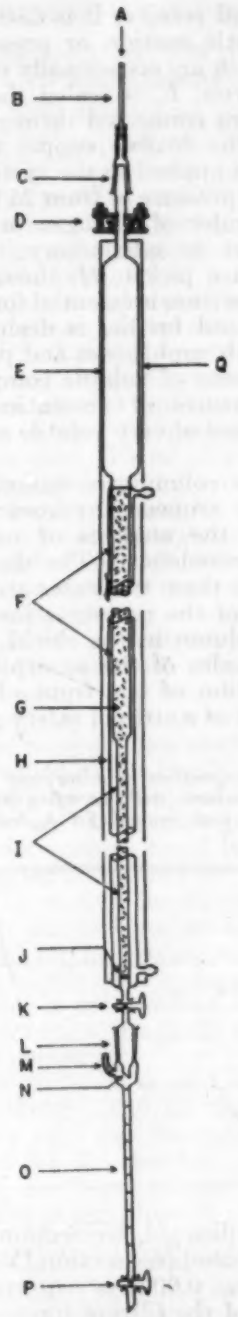

FIGURE 1.—*Apparatus for the analysis by adsorption of mixtures containing aromatic and monoolefin hydrocarbons with paraffins and naphthenes.*

See the text for the significance of the letters, and see table 1 for the dimensions of the various parts.

the vent, *M*, of the 1.1-ml receiver it is desirable to attach a rubber tube through which gentle suction or pressure may be applied to dislodge gas bubbles, which are occasionally entrapped in the receiver. To the top of the reservoir, *E*, is sealed the spherical ground joint (18/9), *D*, which is in turn connected through the soldered metal-to-glass joint *C* [4], with the flexible copper tubing (⅛ in. o. d.), *B*, through which pressure is applied to the system. It is also necessary that a source of inert gas pressure of from 25 to 50 lb/in.^{2} be available. For this purpose a cylinder of nitrogen or carbon dioxide with a pressure regulating valve is satisfactory. The column shown in figure 1 is provided with a jacket, *H*, through which cooling water may be passed. This provision is essential for the analysis of mixtures containing monoolefins, and further is desirable for the analysis of mixtures of aromatics with naphthenes and paraffins if these mixtures contain appreciable amounts of volatile components such as pentane or isopentane. For mixtures of aromatics with naphthenes and paraffins, and in the absence of very volatile components, refrigeration is unnecessary.

The dimensions of the column recommended for the analysis of mixtures containing only aromatic hydrocarbons are different from those recommended for the analysis of mixtures containing substantial quantities of monoolefins. The dimensions of the various parts of the apparatus for these two cases are given in table 1. As a safety measure, because of the pressures involved, it is desirable to mount the adsorption column in the shield, *Q*. This shield should surround the front and sides of the adsorption column, and should provide for the observation of the front of the column. A satisfactory shield may consist of a strip of safety glass in a suitable frame.

TABLE 1.—*Dimensions and capacities of adsorption apparatus for (A) mixtures containing aromatic hydrocarbons with paraffins and naphthenes and (B) mixtures containing aromatic and monoolefin hydrocarbons with paraffins and naphthenes*

	Mixture	
	A	B
Approximate mass of adsorbent (silica gel) ..... g	160	150
Volume of reservoir ..... ml	200	200
Section F, inside diameter ..... mm	22	15
Section F, inside length ..... mm	500	750
Section I, inside diameter ..... mm	10	10
Section I, inside length ..... mm	750	1000
Receiver 1, volume ..... ml	1.1	1.1
Receiver 1, length ..... mm	200	200
Receiver 1, graduations ..... ml	0.01	0.01
Receiver 2, volume ..... ml	11	.....
Receiver 2, length ..... mm	200	.....
Receiver 2, graduations ..... ml	0.1	.....

The adsorbent used is silica gel (see section IV–1, c). The desorbing liquid may be ethyl alcohol (see section IV–1, e). A refractometer having a precision of about 0.0001 is required for the determination of the refractive indices of the filtrate fractions. The refractometer preferably should be equipped with a slot to permit the introduction of volatile fractions without opening the prisms.

IV. METHOD AND RESULTS

1. AROMATIC HYDROCARBONS IN MIXTURES WITH PARAFFINS AND NAPHTHENES

(a) PROCEDURE

The appropriate adsorption column (see table 1) is filled with silica gel and packed by tapping throughout its length with a rubber-covered wooden rod. The packing and filling is continued until the level of silica gel decreases less than 5 mm in 5 minutes of packing and the final height of the silica gel is about 2 to 5 cm below the bottom of the reservoir. The time required to pack a column is about 20 minutes. If the column is not to be used immediately, the silica gel is closed off from the moisture of the atmosphere. The column is then mounted in the shield, *Q*, and the receiver attached.

For the concentration range 0 to 80 percent by volume of aromatic hydrocarbon, a volume of solution sufficient to contain about 20 ml of aromatic hydrocarbon is used for each analysis, except that not less than 30 ml nor more than 125 ml of solution is used. For the concentration range 80 to 100 percent by volume of aromatic hydrocarbon, the solution preferably should be diluted with one-fifth its volume of an aromatic-free paraffin, naphthene, or paraffin-naphthene mixture, and a 30-ml portion of this diluted solution used.[3] The volume selected for the analysis is introduced into the reservoir. The smaller volumes may be introduced with a pipette, which can be inserted through the neck of the reservoir, care being taken not to wet the upper portion of the reservoir. Pressure of 5 to 10 lb/in.^{2} is then applied. When the sample has completely entered the silica gel (which should take about 10 to 20 minutes for the 30- to 50-ml portions), the pressure is reduced, the reservoir opened, and a layer of 1 to 2 cm of silica gel added. The reservoir is then filled with ethyl alcohol and the necessary pressure applied, which is 15 to 50 lb/in.^{2}, depending on the particle size of the silica gel and the viscosity of the hydrocarbon portion and desorbing liquid (sections IV–1, c and 1, d). When a fraction has collected in the receiver, the flow from the adsorption tube is interrupted by closing the stopcock. The volume in the receiver is measured and the fraction withdrawn. A standard procedure should be adopted for measuring and withdrawing fractions. About 40 seconds should be allowed for the upper parts of the receiver to drain before the volume is read and an equal interval allowed for drainage after the withdrawal of the bulk of the fraction before the stopcock on the receiver is closed.[4]

In cases where from 30 to 50 ml is used for the analysis, a receiver of 1.1-ml capacity is sufficient, and all the fractions may be taken approximately equal to 1 ml. For the more dilute solutions, where more than 50 ml is used for the analysis, the collection of so many fractions is tedious and an 11-ml receiver may be used to collect fractions until close to the point where it is estimated that aromatic

[3] For solutions containing appreciably more than 80 percent by volume of aromatic hydrocarbon, the volume intermediate between the aromatic and nonaromatic portions is more than the 1 to 2 ml customarily obtained with more dilute solutions and with the appropriate silica gel (sections IV–1, c and 1, d). In this instance, the liquid front is a very short distance from the boundary between the aromatic and nonaromatic portions, and the heat of wetting is not dissipated before that boundary reaches the warm region. It may be that convection produced by the thermal gradient is responsible for this lack of sharpness in the "break" with very concentrated solutions. In some cases no fraction completely free from aromatic material is produced, and it is for this reason that concentrated solutions should be diluted before analysis.

[4] If stopcock *K* is opened too rapidly, gas bubbles may be trapped in the 1.1 ml receiver. In this event, the stopcock may be closed temporarily and the bubbles displaced by applying suction to the rubber tube attached to *M*.

material will appear in the filtrate. At this point, it is necessary to change to a 1.1-ml receiver.[5] When a sufficient amount of the desorbing liquid has collected the experiment can be discontinued.[6] It is not necessary to determine the refractive index of every fraction, only the refractive indices of those fractions required to locate the plateaus (see fig. 3), and the breaks between them need be determined. The volumes of the components are then determined and the volume percentage computed by using for the total volume the volume of material actually recovered.

During the experiment the pressure should be adjusted so that the rate of flow of filtrate from the column does not exceed about 40 ml/hr when the 11 ml-receiver is used and about 20 ml/hr when the 1.1-ml receiver is used. Rates of flow much higher than these values do not leave adequate time for drainage and the precise determination of the volume of the filtrate fractions. As the rate of flow decreases as the experiment progresses and ethyl alcohol substitutes itself for the original hydrocarbon portion (section IV–1, d), a constant pressure throughout the experiment will give (for solutions of low aromatic content) rates of flow of about 30 to 40 ml/hr at the beginning of the experiment and of about 20 ml/hr toward the end of the experiment. The total time required for an experiment varies from about 3 hours for solutions of high aromatic content to about 6 hours for solutions of low aromatic content. Of this time, about 1½ to 2 hours is required for the liquid to reach the bottom of the column and about 1½ to 4 hours for the collection of the fractions of filtrate.

After an experiment, the adsorbent is found to be tightly packed in the column and cannot be removed by simple tapping. Flushing with water will, however, readily remove the adsorbent. To do this, the column is placed in a reclining position with the top slightly lower than the bottom. A metal tube, which is flexibly connected to the water main and from which a stream of water is issuing, is then inserted in the column and gently forced throughout its length. The silica gel is displaced and flows with the water out of the column.

In future work, it is intended to reactivate the silica gel in the adsorption column. This will save the time required for packing and unpacking the column and will have the further advantage that the silica gel will not come in contact with the moisture of the atmosphere during the filling operation. Reactivation of the silica gel is accomplished by heating it to 180° to 200° C in a slow stream of inert gas.

(b) DIMENSIONS OF THE ADSORPTION COLUMN

A number of adsorption columns of different dimensions were tried in preliminary experiments with lot II of silica gel (see section IV–1, c). These included long narrow columns (260 cm long, 0.9 cm inside diameter) and short wide columns (76 cm long, 2.2 cm inside diameter). Satisfactory results were obtained with the long, narrow columns, the volume of material intermediate between the nonaromatic and the aromatic portions being small and amounting to about 1 to 2 ml. However, this length of column is cumbersome to handle (particularly

[5] Where only one receiver is used and where approximately the same size of fraction is withdrawn throughout, it is not necessary to know the absolute volume of the receiver. Where two receivers are used it is necessary to know the volume of one in terms of the other.

[6] As stated in section IV–1, e, it is possible to see the boundary between the desorbing liquid and the hydrocarbon portion. About 3 ml should be collected after this boundary has passed out of the column.

in removing the silica gel), and a considerable time is required for the hydrocarbon portion to reach the bottom of the column. With the short, wide column the volume of material intermediate between the nonaromatic and the aromatic portion is comparatively large, and a pure aromatic portion is not obtained. The column finally selected for this method of analysis consists of two sections sealed together, the upper section being 50 cm long and 2.2 cm inside diameter and the lower section being 75 cm long and 1.0 cm inside diameter (see table 1). This column, when used with silicia gel of proper particle size, has a capacity and fractionating length sufficient to separate about 20 ml of aromatic hydrocarbon from mixtures with aromatic contents from 20 to 100 percent by volume and somewhat less than 20 ml for lower concentrations. Under these conditions, the volume of material intermediate between the aromatic and nonaromatic portion is usually from 1 to 2 ml for solutions containing less than 80 percent by volume of aromatic hydrocarbon.[7]

(c) EFFECT OF PARTICLE SIZE OF THE ADSORBENT

Experiments were performed with four lots of silica gel. Three of these lots were used as received from the manufacturer. The number given by the manufacturer to designate the type of silica gel, together with the particle size are recorded below for these three lots. The fourth lot was prepared in this laboratory by further treatment of lot III.

Lot	Manufacturer's[8] designation	Particle size[9] (U. S. Standard Sieve)
I	659528—2000	No. 28 to No. 200.
II	6595150—	100% through No. 150, 41% through No. 325.
III	6595150—	100% through No. 150, 0% through No. 325.

Experiments with lot I showed that this material, with the natural rate of flow obtained with no external pressure, was too coarse to give satisfactory results. The break between the aromatic and the nonaromatic portion was not sharp, and the aromatic portion was not free from nonaromatic material. Lots II and III differed considerably in the distribution of their particle size, as indicated. The second lot of adsorbent was satisfactory at all rates of flow tested (see section IV–1, d), the volume intermediate between the nonaromatic and the aromatic portion amounting usually to not more than 1 or 2 ml. The third lot of silica gel was not satisfactory at any rate of flow tested (see section IV–1, d); the break between the aromatic and nonaromatic portions was not sharp and the aromatic portion contained some nonaromatic material. That the unsatisfactory behavior of lot III was due entirely to its lack of very fine material was established by determining first that the adsorptive capacity of lots II and III were essentially the same, and then by grinding some of lot III, reactivating the ground material,[10] and thereby preparing lot IV, which proved to be as satisfactory as lot III.[11]

[7] See footnote 3.
[8] Davison Chemical Corporation, Baltimore, Md.
[9] The values for the No. 150 sieve are the manufacturer's specifications, whereas the values for the No 325 sieve were determined by the Bureau's Cement and Concreting Materials Section.
[10] Necessary only to remove moisture adsorbed during the grinding process.
[11] Silica gel with satisfactory characteristics may be obtained from the Davison Chemical Corporation, Baltimore, Md., under the number "6595150—50% through No. 325."

(d) EFFECT OF RATE OF FLOW

The rate of flow depends on the particle size of the adsorbent, the density of packing of the column, the viscosity of the hydrocarbon sample, the viscosity of the desorbing liquid, and the pressure applied to the column. When lot II of silica gel (section IV–1, c), was used, with hydrocarbons of the gasoline range and the natural rate of flow obtained with a head of 15 cm of desorbing liquid (dimethyl furane), the average rate at which the front of liquid travelled down the column was about 5 cm/hr, being higher than this value in the upper portion of the column and lower than this value toward the bottom of the column. With a gage pressure of 20 lb/in.^{2} and ethyl alcohol as the desorbing liquid, the average rate at which the front of liquid travelled down the column was about 80 cm/hr, being substantially higher than this value in the upper portion, and decreasing toward the bottom of the column.[12] The results obtained for these diverse rates of flow were not significantly different, in both cases the volume intermediate between the nonaromatic and the aromatic portions being about 1 to 2 ml. With lot III of silica gel (section IV–1, c) and a gage pressure of 20 lb/in.^{2} the average rate at which the front of liquid travelled down the column was about 240 cm/hr. For this lot of silica gel, at average rates of flow of 240, 100, and 25 cm/hr, the results were unsatisfactory, the volume intermediate between the nonaromatic and aromatic portions amounting to 5 to 8 ml and the aromatic portion containing some nonaromatic material. When lot IV of silica gel and a gage pressure of 45 lb/in.^{2} was used, the average rate at which the front travelled down the column was 90 cm/hr, the volume intermediate between the nonaromatic and the aromatic portions being 1 to 2 ml.

From the above experiments, it is evident that the sharpness of the separation does not depend significantly on the rate of flow within the range investigated. The upper limit at which it is satisfactory to operate depends instead in the time required for the precise determination of the volume of the filtrate fractions (section IV-1, a) and is about 20 ml/hr during the collection of the aromatic portion toward the end of the analysis. For each lot of silica gel which is sufficiently fine (but not so fine that excessively high pressures are required), the pressure required to give a rate of flow of 20 ml of filtrate per hour toward the end of the experiment can be determined and used in subsequent analyses.

(e) DESORBING LIQUID

Experiments were performed with the following desorbing liquids: Methyl alcohol, ethyl alcohol, propyl alcohol, acetone, methyl ethyl keytone, diethyl ether, and dimethyl furane. With the exception of dimethyl furane, the boundary between the desorbing liquid and the hydrocarbon portion is plainly visible.[13] In the case of diethyl ether, acetone, and methyl ethyl ketone the boundaries between the desorbing liquid and the hydrocarbon portion are not normal to the walls of

[12] As filtrate issues from the column, and ethyl alcohol replaces the original hydrocarbon portion, the rate of flow decreases because ethyl alcohol has a higher viscosity than the average for hydrocarbons of the gasoline range. On the other hand, with higher boiling fractions, such as kerosine, etc., the rate of flow may be expected to stay constant or increase slightly as ethyl alcohol replaces the original hydrocarbon portion. As each milliliter of liquid occupies a length of about 2 cm in the packed section with 1.0 cm inside diameter, a rate of movement of the liquid front of 40 cm/hr corresponds to a rate of flow of filtrate of about 20 ml/hr.

[13] In many experiments it is also possible to see the boundary between the aromatic and the nonaromatic portion.

the column but are irregular and frequently extend over a length of 5 to 10 cm. In the case of methyl alcohol two phases are present in one or more fractions toward the end of the experiment.[14] The occurrence of two phases makes difficult if not impossible the accurate determination of the volume of aromatic hydrocarbon. With ethyl alcohol and propyl alcohol, the boundaries between the desorbing liquid and the hydrocarbon portion are substantially normal to the walls of the column and only one phase occurs, at least with hydrocarbons of the gasoline range.[15] Owing to its higher viscosity, the rate of filtration with propyl alcohol for a given applied pressure is much slower than with ethyl alcohol. Fairly satisfactory results were obtained with dimethyl furane.

(f) EXPERIMENTAL RESULTS

The result of an experiment [16] with a solution containing a paraffin hydrocarbon (2,2,4-trimethylpentane) and a naphthene hydrocarbon (methylcyclohexane) is shown in figure 2. It is apparent that the

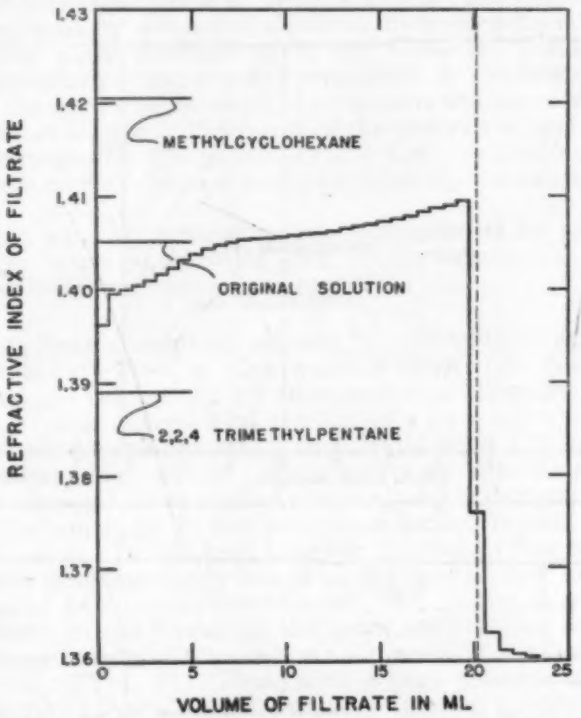

FIGURE 2.—*Experiment with a paraffin and a naphthene hydrocarbon.*

The scale of ordinates gives the refractive index, n_D^{25}, of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The plot refers to an experiment in which 20 ml of solution containing equal volumes of 2,2,4-trimethylpentane and methylcyclohexane was used.

[14] Since aromatic hydrocarbons of the gasoline range are completely soluble in methyl alcohol, it is evident that sufficient water has been displaced from the silica gel by the methyl alcohol to cause the appearance of two phases. This behavior has been observed previously [5].

[15] Ethyl alcohol was used as the desorbing liquid in two experiments with material from the kerosine range. In one case with material containing substantially no aromatic hydrocarbons two phases were observed, whereas in the other case with material of relatively high aromatic content (15 percent) only one phase was produced. The appearance of two phases in the first case is doubtless due to the limited solubility of paraffins and naphthenes of the kerosine region in ethyl alcohol.

[16] This experiment, together with two of the analyses given in table 2 were made by A. J. Streiff.

separation of paraffins from naphthenes with the apparatus and procedure in question is small enough to permit these two classes to be grouped together in the results from an analysis.

The results of analyses that are typical are shown for two solutions of known aromatic content in figure 3, *A* and *B*. The refractive indices of the fractions in the plateaus agree with the refractive indices of the pure components within 0.0001. The volume intermediate between substantially nonaromatic and substantially aromatic material is about 1 to 2 ml, and the volume intermediate between substantially aromatic material and the desorbing liquid (ethyl alcohol) is about the same. The accuracy obtainable when this method is applied to synthetic mixtures is indicated by the data in table 2.

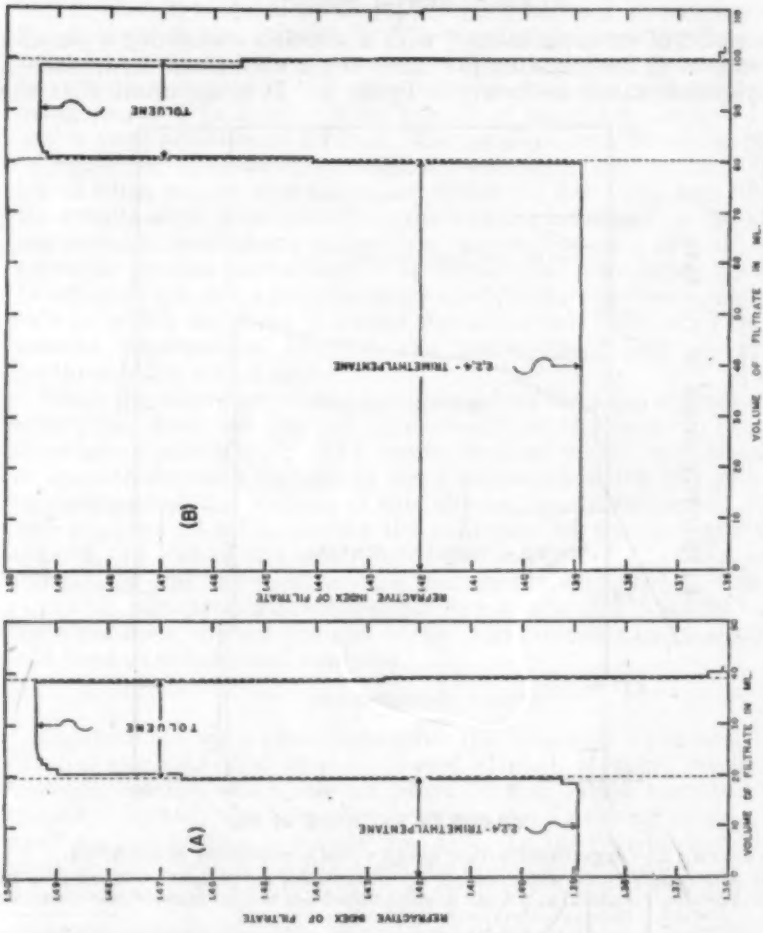

FIGURE 3.—*Analyses of mixtures containing aromatic and paraffin hydrocarbons.*

The scale of ordinates gives the refractive index, n_D^{25}, of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. *A*, an analysis in which approximately 40 ml of a solution containing 49 and 51 percent by volume of toluene and 2,2,4-trimethylpentane, respectively, was used; *B*, an analysis in which approximately 100 ml of a solution containing 20 and 80 percent by volume of toluene and 2,2,4-trimethylpentane, respectively, was used. For experimental details, see text.

TABLE 2.—*Comparison of values for the composition of five solutions, as given by synthesis and as determined analytically*

Solution	Components	Composition by—	
		Synthesis	Analysis
		% *by volume*	% *by volume*
1	Toluene	3.990	4.053
	2,3,4-trimethylpentane	96.00	95.95
2	Toluene	22.20	22.45
	2,2,4-trimethylpentane	77.80	77.55
3	Toluene	49.95	49.92
	2,2,4-trimethylpentane	50.05	50.08
4	Toluene	79.91	79.89
	2,2,4-trimethylpentane	20.09	20.11
5	Toluene	92.49	92.45
	2,2,4-trimethylpentane	7.51	7.55

FIGURE 3.—*Analyses of mixtures containing aromatic and paraffin hydrocarbons.*

The scale of ordinates gives the refractive index, n_D^{25}, of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. Curve 1 was obtained with a 40 to 60 percent by volume solution of toluene and 2,2,4-trimethylpentane, respectively. Curve 2, a 40 to 60 percent by volume solution of the same components, respectively. Curve 3, a 50 to 50 percent by volume solution of the same components, respectively. Curve 4, a 20 to 80 percent by volume solution of the same components, respectively. Curve 5, a 7.5 to 92.5 percent by volume solution of the same components, respectively.

The result of the analysis of an aviation gasoline containing approximately 16 percent by volume of aromatic hydrocarbons is shown in figure 4. The small fluctuations in the refractive indices of the naphthene-paraffin portion are due principally to the loss of volatile compounds during the collection of the fractions and the measurement of the refractive indices. The result of the analysis of material from the kerosine range (bp 166 to 290° C at 1 atm), containing approximately 15 percent by volume of aromatic material, is shown in figure 5.

2. AROMATIC AND MONOOLEFIN HYDROCARBONS IN MIXTURES WITH PARAFFINS AND NAPHTHENES

(a) PROCEDURE

The appropriate adsorption column (see table 1) is prepared as described in section IV–1, a. Ice water is allowed to flow through the jacket of the column for 10 minutes before the introduction of the sample.[17] A measured 5-ml portion of a paraffin, a naphthene, or a paraffin-naphthene mixture is then added from a pipette to the top of the adsorption column. When nearly all of this material has entered the silica gel, the sample to be analysed is introduced from a pipette. The remainder of the analysis is similar to that described in section IV–1, a. In this case, however, the rate of flow for a given gage pressure is substantially less than the rate of flow obtained in the analysis of aromatic hydrocarbons. This is due in part to the higher viscosity of the liquids at the lower temperature and in part to the decrease in rate of filtration with increase in the length of the column (section IV–1, d). Thus, with a gage pressure of 30 to 35 lb/in.^{2}, when lot II of silica gel was used (section IV–1, c), it was found that 4 to 5 hours were required for the liquid to reach the bottom of the column, the rate of flow of the filtrate being about 10 ml/hr. The column recommended for this analysis is longer than that recommended for aromatics in mixtures with paraffins and naphthenes. The additional length appears to be necessary to effect the separation of paraffin-naphthene material from monoolefins, and of monoolefins from aromatics. This column will separate about 10 ml of mo-

[17] If brine or any other refrigerating fluid at −10° to −20° C is available, it should preferably be used.

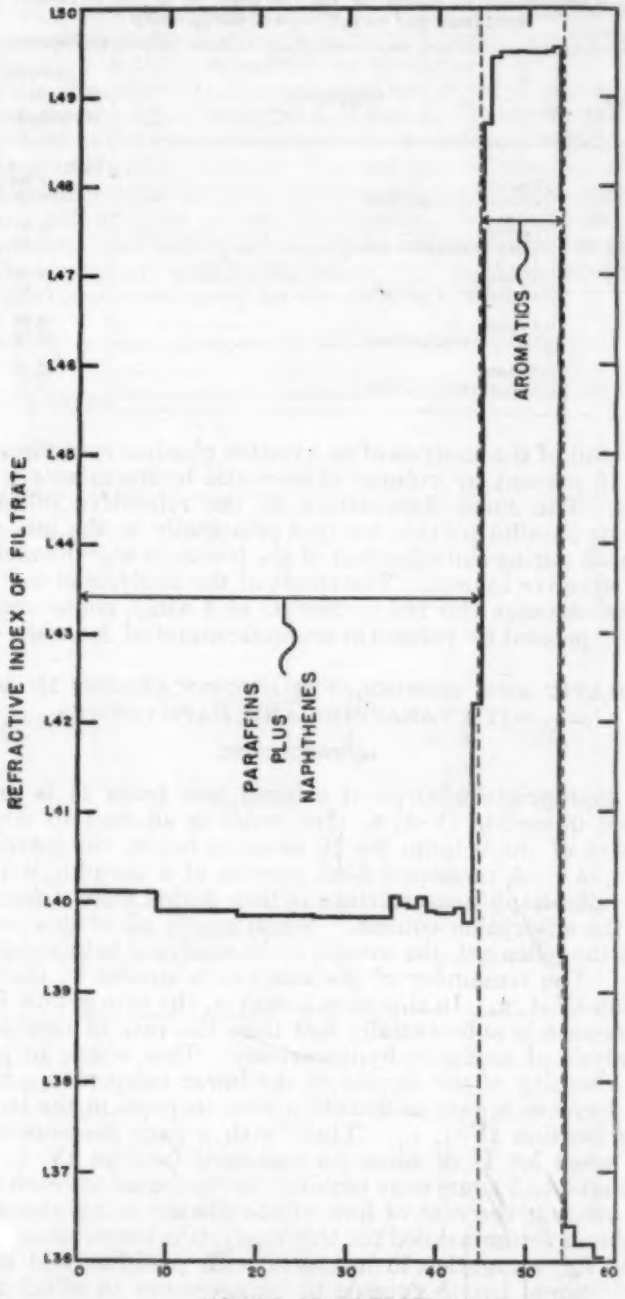

FIGURE 4.—*Analysis of an aviation gasoline.*

The scale of ordinates gives the refractive index, n_D^{25}, of the filtrate, and the scale of abecissas gives the volume of the filtrate in milliliters. The plot refers to an analysis in which approximately 55 ml of aviation gasoline was used.

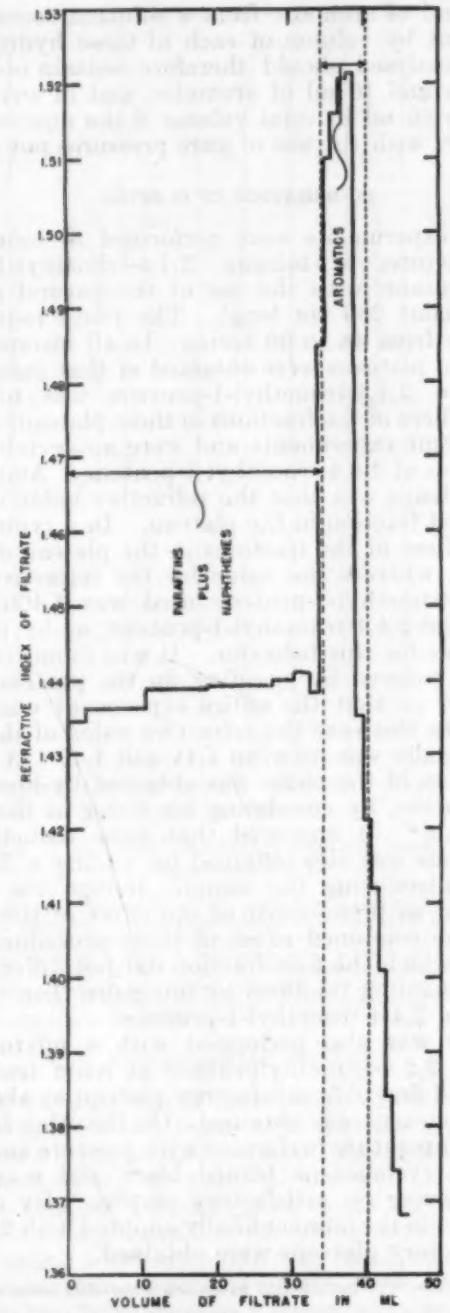

FIGURE 5. *Analysis of a kerosine fraction.*

The scale of ordinates gives the refractive index, n_D^{25}, of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The plot refers to an analysis in which approximately 40 ml of a kerosine sample (bp, 166° to 290° C) was used.

noolefin and 10 ml of aromatic from a solution containing approximately 30 percent by volume of each of these hydrocarbons. The solution to be analysed should therefore contain not more than 10 ml of monoolefin and 10 ml of aromatic, and in any event should not exceed 50 to 60 ml in total volume if the analysis is to be performed in 9 hours with the use of gage pressures not in excess of 50 lb/in ^{2}.

(b) BEHAVIOR OF OLEFINS

A number of experiments were performed at room temperature with known mixtures of toluene, 2,4,4-trimethyl-1-pentene, and 2,2,4-trimethylpentane, with the use of the natural rate of flow in long columns (about 260 cm long). The times required for these experiments were from 48 to 60 hours. In all instances plateaus or approximations to plateaus were obtained at that part in the volume of filtrate where 2,4,4-trimethyl-1-pentene was to be expected. The refractive indices of the fractions in these plateaus were, however, different in different experiments and were appreciably higher than the refractive index of 2,4,4-trimethyl-1-pentene. Another characteristic of these plateaus was that the refractive index decreased from the first to the last fraction in the plateau. In a typical experiment, the refractive indices of the fractions in the plateau decreased from 1.4324 to 1.4217, whereas the value for the refractive index of the sample of 2,4,4-trimethyl-1-pentene used was 1.4063. It appears that reaction of the 2,4,4-trimethyl-1-pentene, as by polymerization, may be responsible for this behavior. It was found that this "polymerization" was reduced by speeding up the process by the application of pressure so that the entire experiment was performed in about 6 hours. In this case the refractive index of the first fraction in the plateau usually was between 1.41 and 1.42. A further reduction in the reaction of the olefin was obtained by lowering the temperature of operation, by circulating ice water in the jacket of the adsorption column.[18] It appeared that some reduction in the reaction of the olefins was also obtained by adding a 5-ml portion of paraffin before introducing the sample, though the effect of this procedure was not so pronounced as the effect of the two foregoing procedures.[19] The combined effect of these procedures was to produce plateaus in which the first fraction did not differ by more than 0.004 and the remaining fractions by not more than 0.003 from the refractive index of 2,4,4-trimethyl-1-pentene.

An experiment was also performed with a mixture of toluene, cyclohexene, and 2,2,4-trimethylpentane at room temperature with the natural rate of flow. A satisfactory plateau at about the refractive index of cyclohexene was obtained. On the other hand, in experiments at room temperature performed with pressure and a more rapid rate of flow, the cyclohexene turned black and mingled with the toluene portion giving no satisfactory plateau. By operating near 0° C with pressure, in the manner finally adopted with 2,4,4-trimethyl-1-pentene, satisfactory plateaus were obtained.

[18] Small scale tests made at −76° C indicate that no reaction of the olefin occurs at this temperature in 24 hours.

[19] When the front of hydrocarbon comes in contact with fresh silica gel, a substantial rise in temperature takes place. The introduction of the paraffin hydrocarbon before the sample allows time for this heat of wetting to be dissipated before the olefin reaches that portion of silica gel. The paraffin hydrocarbon also displaces a substantial part of the air from the tube and may in this way help to reduce the reaction of the olefins. Removal of oxygen by evacuation of the column would also serve to reduce the reaction of olefins. However, the complete evacuation of the column described here is a slow process and appears impracticable.

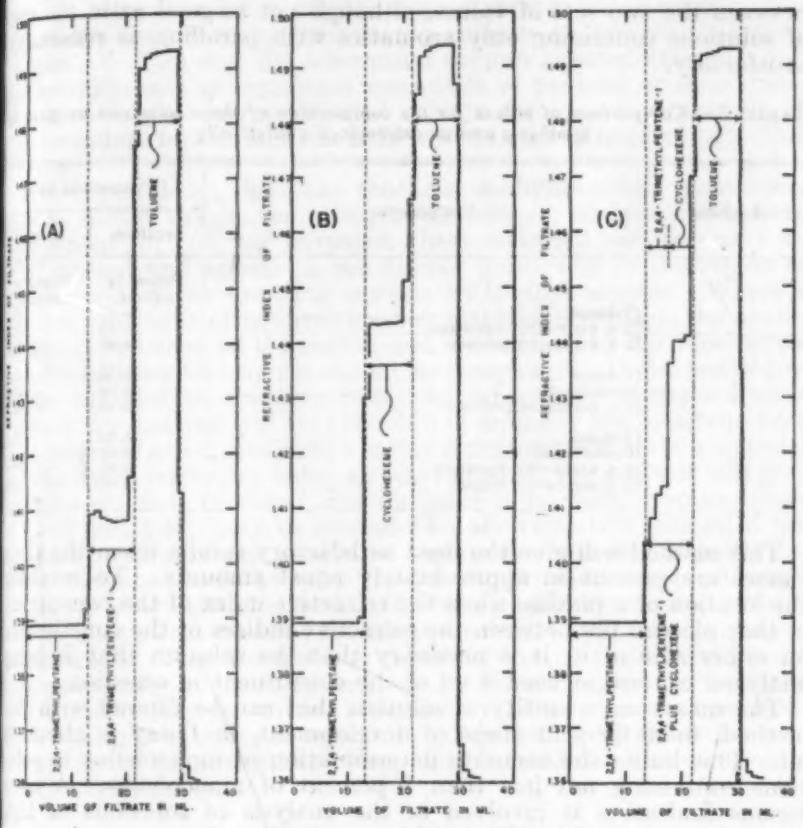

FIGURE 6.—*Analyses of solutions containing aromatic, monoolefin, and paraffin hydrocarbons.*

The scale of ordinates gives the refractive index, n_D^{25}, of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. *A*, an analysis in which approximately 25 ml of a solution containing equal volumes of toluene, 2,4,4-trimethyl-1-pentene, and 2,2,4-trimethylpentane was used; *B*, an analysis in which approximately 25 ml of a solution containing equal volumes of toluene, cyclohexene, and 2,2,4-trimethylpentane was used; *C*, an analysis in which approximately 25 ml of a solution containing one-third toluene, one-sixth cyclohexene, one-sixth 2,4,4-trimethyl-1-pentene, and one-third 2,2,4-trimethylpentane was used. In all three analyses 5 ml of 2,2,4-trimethylpentane was introduced into the adsorption column prior to the introduction of the solution.

(c) EXPERIMENTAL RESULTS

The results of the analyses of three solutions are shown in figure 6 *A*, *B*, and *C*. It is evident from these that the separation of each of the three classes of hydrocarbons from one another is reasonably sharp. The characteristic decrease in the refractive index at the 2,4,4-trimethyl-1-pentene plateau (section IV–2, b) is noticeable (*A*.). The cyclohexene plateau, however, does not show this behavior (*B*). It is interesting to observe (*C*) that there was a separation of 2,4,4-trimethyl-1-pentene and cyclohexene and that the relative amounts of these two substances in a mixture can be estimated from an experiment of this type. The values for the amounts of the constituents of these solutions as given by synthesis and as determined analytically are given in table 3. It will be seen that the agreement

between the two sets of values, although not as good as in the case of solutions containing only aromatics with paraffins, is reasonably satisfactory.

TABLE 3.—*Comparison of values for the composition of three solutions as given by synthesis and as determined analytically*

Solution	Components	Composition by—	
		Synthesis	Analysis
		Percent by volume	*Percent by volume*
1	Toluene	33.33	33.
	2, 4, 4-trimethyl-1-pentene	33.33	33.
	2, 2, 4-trimethylpentane	33.33	33.
2	Toluene	33.33	33.
	Cyclohexene	33.33	33.
	2, 2, 4-trimethylpentane	33.33	33.
3	Toluene	33.33	33.
	Cyclohexene	16.67	33.
	2, 4, 4-trimethyl-1-pentene	16.67	
	2, 2, 4-trimethylpentane	33.33	33.

This method will give the most satisfactory results when the three classes are present in approximately equal amounts. To establish the location of a plateau when the refractive index of the constituent in that plateau lies between the refractive indices of the constituents on either side of it, it is necessary that the solution that is being analyzed contain at least 4 ml of the constituent in question.

The maximum quantity of solution that can be filtered with this method, in its present stage of development, in 1 day is about 60 ml. This limits the accurate determination of monoolefins to solutions containing not less than 7 percent of monoolefins. A more serious limitation is involved in the analysis of solutions of high aromatic content. As the maximum quantity of aromatic that can be separated from solutions containing olefins is of the order of 15 to 20 ml, it is not possible to use more than about 20 ml of sample of high aromatic content for an experiment. In order that 4 ml of monoolefin be obtained such a sample must contain 20 percent of monoolefin. Where possible, the composition of the solution to be analyzed should be brought to approximately the optimum composition by adding to it known amounts of hydrocarbons from the requisite classes.

V. RECOMMENDED PROCEDURE FOR THE DETERMINATION OF THE AROMATIC CONTENT OF A STRAIGHT-RUN PETROLEUM DISTILLATE

The aromatic content of the sample to be analyzed is estimated roughly. In the absence of information as to the source of the material, this estimate may be made from a consideration of the refractive index of the sample or from the results of a preliminary experiment (which requires only 10 to 15 minutes) in which a few milliliters of sample is filtered through a few grams of silica gel (No. 28 to No. 200 U. S. Standard Sieve) and the difference between the refractive index of the first drop of filtrate (which should be aromatic free)

and the refractive index of the original sample obtained [6]. The size of the sample to be used in the analysis is then decided upon (section IV–1, a) and the adsorption column selected (table 1). If the sample contains significant quantities of pentane or isopentane, it is necessary to use a jacketed column for operation near 0° C. The procedure for the analysis is the same as that described in section IV–1, a.

If the petroleum distillate contains nonhydrocarbon substances such as sulfur, oxygen, or nitrogen compounds, or dyes which have been added for coloring purposes, these materials are displaced by ethyl alcohol and appear in the filtrate principally in the region of the junction of the aromatic portion with ethyl alcohol. Where a significant amount of nonhydrocarbon material is present, the analysis should be corrected if possible, and if not possible, the uncertainty introduced from this source should be recognized. If the nonhydrocarbon material has the same refractive index as the aromatic hydrocarbons, the analysis will give the sum of aromatic hydrocarbons plus the nonhydrocarbon material; whereas if the nonhydrocarbon material has the same refractive index as ethyl alcohol, the analysis will give only the aromatic content. For the gasoline fraction, average values of 1.496 and 1.482 may be assumed for the refractive indices of the aromatic hydrocarbons and the sulfur compounds, respectively. When compared with the value 1.360 for the refractive index of ethyl alcohol, it is evident that each milliliter of sulfur compound present will have an effect on the analysis equivalent to 0.9 ml of aromatic hydrocarbon. For the gasoline fraction, the correction for sulfur compounds may be made by determining the percentage by weight of sulfur, multiplying the value obtained [20] by 3.7 to convert to percentage by volume of sulfur compounds and deducting 0.9 times the percentage by volume of sulfur compounds from the uncorrected value for the aromatic content.

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[6] A. R. Glasgow, Jr., and F. D. Rossini, A. P. I. Research Project 6, National Bureau of Standards. Unpublished data.

WASHINGTON, November 1, 1944.

[20] This factor is obtained by assuming that each sulfur compound had 1 atom of sulfur per molecule, that the average molecule weight of the sulfur compounds is 130, and that the average density of the sulfur compounds is 0.83.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1653

Part of Journal of Research of the National Bureau of Standards, Volume 34, May 1945

METHODS FOR THE EVALUATION OF ANALYTICAL FILTER PAPERS

By B. W. Scribner and W. K. Wilson

ABSTRACT

As part of an investigation of analytical filter papers for the purpose of assisting in the development of standards of quality, improved methods for rate of flow of water, retention of fine precipitates, and determination of ash were developed. The use of complicated apparatus for measuring the rate of flow of water was avoided by applying Darcy's law to the ordinary conical filter. The use of prefiltered water in making the measurement was found necessary for satisfactory reproducibility. As the standard method for determining the ash content of paper is not sufficiently accurate for filter paper, the method was modified in that a tare crucible is used and the test specimen wetted and pressed into a compact wad to permit the use of as small a crucible as possible.

The other tests were bursting strength of wet paper, thickness, weight per unit area, alpha cellulose, copper number, and acidity (pH). The last three named are of importance relative to the purity of the cellulose and the stability of acid-washed papers, as instances of deterioration of the cellulose of such papers have been observed. Action of acid results in brittling of the papers and in the formation of modified forms of cellulose that are soluble in some solutions.

CONTENTS

	Page
I. Introduction	453
II. Testing methods	454
1. Retentiveness to fine precipitates	454
2. Flow of water	454
3. Content of ash	456
4. Bursting strength of wet paper	457
5. Thickness, weight, and density	457
6. Stability	457

I. INTRODUCTION

As a part of an investigation at the National Bureau of Standards to establish standards for analytical filter papers, testing procedures for determination of their quality have been developed. It is believed that the various tests are adequate for the evaluation of properties of importance in ordinary analytical work. The tests are being applied to nearly all types and grades of papers, both foreign and domestic, now available in this country, and experience has indicated that the tests are suitable for effecting a standardization of quality for analytical filter papers. When additional testing is completed, the issuance of a report dealing with quality standards is contemplated.

Improved methods were developed for testing for retention of barium sulfate, rate of flow of water through the papers, and content

of ash. A method was also developed for determination of the bursting strength of wet paper. The following additional testing methods are used. These are standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI),[1] and the Association's designations of the methods are included.

Thickness (T 411 m) and weight in grams per square meter (T 410 m). Density is calculated from these values.

Alpha cellulose (T 429 m), copper number (T 430 m) and acidity as pH (T 435 m). These are related to the purity of the cellulose and the stability of the papers.

Discussions and descriptions of the methods follow.

II. TESTING METHODS

1. RETENTIVENESS TO FINE PRECIPITATES

The use of a precipitate of barium sulfate is a time-honored practice for testing filter papers for retentiveness to fine precipitates, and it appears to be satisfactory for the purpose. However, it is necessary that the following instructions be followed exactly:

Dissolve 0.55 g of potassium sulfate in 275 ml of water and add 1.0 ml of concentrated hydrochloric acid. This solution contains about 0.1 g of sulfur. Heat to boiling, and while at the boiling temperature, add slowly and with continuous stirring 25 ml of 5-percent barium chloride solution. It is very important to have the specified concentration of acid and to keep the solution at the boiling temperature during the precipitation. Allow to stand without agitation for not less than 2 hours nor more than 6 hours at a temperature below the boiling point and not less than 70° C. Prepare at least four circles of the filter paper in the usual way for filtration, in 60-degree long-stemmed funnels. Stir the precipitate until it is evenly suspended in the liquid and filter approximately 50 ml of the mixture through each circle of paper, collecting the filtrates in 250-ml Erlenmeyer flasks. Swirl the filtrates to bring any sulfate to the center and view from above against a black background for the presence of barium sulfate. The experience at the Bureau is that 0.3 mg or less can be detected in this manner. The paper is considered unsatisfactory if any barium sulfate is seen in the filtrate.

2. FLOW OF WATER

A report on the rate of flow of water through filter paper has already been published as a part of this investigation.[2]

Various forms of apparatus were devised by other investigators, but a satisfactory method was evolved by Bogaty and Carson which does not require the use of special, complicated apparatus, and has the advantage of simulating the manner in which filtrations are made. The filter paper is folded in a cone in the usual way, taking care to expel air pockets, and, to obviate any variable that might be introduced by the use of a funnel, the cone is suspended freely in a wire loop. The change in head and filtering area in the use of a cone introduces no complications because, according to Darcy's law, the

[1] Copies of the TAPPI methods can be obtained from the Association at 122 East 42d St., New York 17, N. Y.

[2] Bogaty, H., and Carson, F. T., Measurement of rate of flow of water through filter paper, J. Research NBS **33**, 353 (1944) RP1613.

rate of filtering of water for a given filter paper is proportional to the area of the filter and to the head of water. With this relation as a starting point it was found possible to derive a simple flow constant applicable to a conical filter, which gives the speed of filtering from a measurement of the time required to filter half the volume of water remaining in the cone (starting with any convenient, known volume).

The water-filtration coefficient, k, is determined by means of the equation

$$k=\frac{1.151 \log \frac{v_1}{v}}{t-t_1},$$

in which $t-t_1$ is the time interval required to decrease the volume of water in the filter cone from v_1 to v. If the measurements are so made that $v=v_1/2$, and t_1 is taken as zero when the volume in the cone is v_1, $k=0.3465/t$ for any value of v_1 that may be chosen. In order to avoid very small numbers, the rate of flow through the filter paper is designated by the coefficient K, where $K=10^4k=3465/t$. K is the number of milliliters of water filtered through a square meter of filter paper in 1 second under a head of 1 centimeter of water.

A phenomenon exhibited by filter paper, and other porous materials, is that ordinarily the rate of flow of liquids through them becomes progressively slower with continued flow. As this led to some discrepancies in results obtained for filter paper, considerable study was made to find the cause of it and means of overcoming its effect. No conclusive explanation as to cause was arrived at, and the same appears to be true of explanations offered by other investigators. However, the difficulty was traced to some unknown condition of water used in making the test, as it was found that the change in rate can be almost eliminated by prefiltration of the water. A description of the method follows.

Prepare distilled water by prefiltering it through filter paper, the rate of flow of which is at least as low as that of the paper to be tested. Use two or more filters in series. For each kind of filter paper to be tested a volume of prefiltered water equal to three or four times the volume of the cone will usually be sufficient. If a considerable quantity of water is to be prepared, the filters should be renewed frequently, because they lose their effectiveness with continued flow of water through them.

Carefully fold a filter circle in the usual way to form a 60-degree cone. Place it in a 60-degree funnel and fill it with water prepared in the manner described. Press down the folds to expel all air pockets and to make the three plies smooth and in good contact. Allow about three-fourths of the water to filter through, then pour off the excess. Save the water to wet the next specimen. Remove the empty cone and suspend it freely over a burette by supporting the cone in a loop of wire of such size that it will support the cone at about two-thirds of the distance from its apex.

Use prefiltered water having a temperature of $23°\pm2°$ C, and pour into the cone, all at once, a known volume which is approximately two-thirds of the volume of the cone. When one-fifth of the water has filtered through into the burette, start a stopwatch. When half the remaining volume has filtered through, stop the stopwatch and record the time in seconds. Test not less than 10 circles, using

the same water over and over and adding to it from the prepared supply as found necessary.

The time required to filter half the volume remaining is an inverse measure of the rate of flow, and is substantially the same for any given filter paper, irrespective of the size of the test specimen. Convenient volumes of water initially poured in for filter circles of the sizes most generally used are as follows:

Diameter of circle	Initial volume
cm	ml
11	25
9	15
7	7.5
5.5	3.5

3. CONTENT OF ASH

The necessity for very accurate determination of ash content, together with the small amount present, requires special modifications of the standard method for testing paper. A large test specimen but as small an ignition crucible as possible are required for good accuracy. These conditions are fulfilled by wetting the filter paper with distilled water, thus permitting compact wadding of the paper for conservation of space. The use of a tare crucible and special precautions in the testing operations are necessary. The details of the method are as follows:[3]

Use 20-ml platinum crucibles with covers. A tare crucible with a cover is carried through all operations exactly the same as the crucibles used for the tests. The tare crucible must have practically the same weight and surface area as the test crucible.

Heat the crucibles and covers in a muffle furnace at approximately 925° C. Cool in a desiccator and weigh to the nearest 0.1 mg. Dry about 6 g of the paper to constant weight at 100° to 105° C and weigh to the nearest 0.01 g. Wet the paper with distilled water containing not more than 10 parts per million of igneous solids, then roll it into a compact mass with clean fingers. Put the test specimen in a crucible, cover it, and place it in a cold muffle furnace. Start the ignition and after smoking has ceased remove the cover and continue the ignition for 2 hours at 925° C. Replace the cover, cool and weigh the crucible and ash. The ignition is considered to be complete when the weight of the ash becomes constant after reignition for 30 minutes. All the cooling must be done in a desiccator, and the test crucibles and tare crucible must be allowed to remain on the balance pans the same length of time. The ash must be protected from air currents at all times.

Duplicate determinations shall be made, and they shall agree within 0.003 percent of the weight of the dry paper. Report the average of the values to the nearest 0.01 mg per 11-cm circle of the paper and to the nearest 0.001 percent of the weight of the dry paper.

[3] The authors acknowledge the assistance of Herbert F. Launer in the development of this method.

4. BURSTING STRENGTH OF WET PAPER

For determination of the strength of filter paper, resistance of wetted paper to bursting appears to be a logical choice. With the exception that the paper is tested after wetting it, the test is made according to the standard method of the Technical Association of the Pulp and Paper Industry, T 403m. The paper is clamped in the testing instrument over a circular orifice through which pressure is applied by a compressed fluid until the paper breaks. The pressure is recorded on a maximum-reading gauge and is reported as "points." The procedure is as follows:

Clip together a pack of five circles of the filter paper, and immerse the pack in distilled water at 23° C for 5 minutes. Remove the pack, allow it to drain suspended for 10 seconds, then immediately determine the bursting strength. Use enough packs to obtain not less than 10 values. Report the average bursting strength to the nearest one-quarter point.

5. THICKNESS, WEIGHT, AND DENSITY

The thicknesses of at least 10 separate circles are determined with a dial micrometer, and the average of the values is reported to the nearest 0.0002 in. For determination of weight, a pack of not less than 10 sheets is weighed on a chemical balance, and the weight is reported as grams per square meter to the nearest 0.1 g. The density is calculated from the thickness and weight, as grams per cubic centimeter to the nearest 0.001 g.

6. STABILITY

Analytical filter paper as produced in the paper mill has a high degree of cellulosic purity, which is a prime requisite for stability of paper, and every care is taken to keep the paper as free as possible from extraneous materials, as impurities, of course, would interfere with analytical determinations. There should be no question, therefore, of the stability of any of the various types of the papers except those treated with acid to reduce the ash to a minimum or to harden the papers. Acids are very deteriorative to cellulose, and unless the treatment with the strong mineral acids is done very carefully, degradation of the cellulose with resultant embrittlement of the paper fibers may occur. Moreover, degraded cellulose is soluble in some solutions, and therefore may pass into filtrates and cause erroneous analytical results.

The Bureau has found in its studies [4] of the deterioration of papers that a high content of alpha cellulose and a low copper number are the best criteria of the purity of the cellulose of paper fibers. Alpha is a term used to designate the part of the cellulose that is insoluble in a strong solution of sodium hydroxide under definitely prescribed conditions. It is the pure or unmodified fraction of the cellulose. The copper number designates the amount of copper precipitated by cellulose under certain conditions from a solution of copper sulfate. It represents the amount of unstable modified forms of cellulose present.

[4] A. E. Kimberly and B. W. Scribner, Summary report of National Bureau of Standards research on preservation of records, Misc. Pub. NBS M154 (1937).

The Bureau has published extensive data showing the close relation of alpha cellulose, copper number, and acidity as hydrogen ion concentration (pH), to the stability of various other kinds of papers. Some information of this kind has been obtained for filter papers. For example, a double acid-washed filter paper that had become brittle during storage had only 72 percent alpha cellulose, a high copper number of 3.3, and a pH value of 4.5. Comparable figures for good paper of the same type and grade are alpha cellulose, 96 percent; copper number, 0.4; and acidity, 6 pH. For good stability, the pH value of paper should not be below 5.

In a few other instances noted at the Bureau, papers that had been double acid-washed were so brittle that they burst when used for filtration, and all of these were characterized also by a poor condition of the cellulose. The bursting strength of some of these papers ranged for dry paper, from 4 to 14 points as compared with around 20 points for underteriorated paper. All the deteriorated papers had been stored under good conditions, and some of them had not been in stock very long.

In view of these experiences with the deteriorated papers, all of which were made by manufacturers of papers that are usually of the highest quality, the use of the recommended tests relating to stability seems desirable for both consumer testing and manufacturing control of acid-washed papers.

WASHINGTON, January 18, 1945.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

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INTRINSIC VISCOSITIES AND OSMOTIC MOLECULAR WEIGHTS OF CELLULOSE ACETATE FRACTIONS

By Arnold M. Sookne and Milton Harris [1]

ABSTRACT

The intrinsic viscosities and osmotically estimated number-average molecular weights of a series of cellulose acetate fractions have been measured. It was found that within the range of chain lengths investigated (number-average molecular weight, $\overline{M}_n$, up to 130,000) the number-average molecular weights are proportional to the intrinsic viscosities in acetone solutions, in agreement with Staudinger's rule and the results of Kraemer. An estimate is provided of the relative homogeneity with respect to molecular size of the fractions and the starting material from which they were prepared.

CONTENTS

	Page
I. Introduction	459
II. Methods	460
1. Viscosity measurements	460
2. Osmotic-pressure measurements	460
III. Results and discussion	461
IV. References	465

I. INTRODUCTION

According to Staudinger's rule, the molecular weight, M, of a linear high polymer is related to its intrinsic viscosity, $[\eta]$, by the expression $[\eta]=KM$, where $[\eta]=\lim_{c\to 0}(\eta_{sp}/c)$, K is a constant, and c the concentration in grams per 100 ml of solution [1].[2] The validity of this relationship has often been questioned, and it has recently been demonstrated that several unbranched polymers do not conform to this rule but rather to the more general relationship $[\eta]=KM^a$, where a is a constant with a value between 0.5 and 2 [2, 3].

Some time ago a series of cellulose acetate fractions was prepared in this laboratory in connection with a study of the mechanical properties of this material [4].[3] The intrinsic viscosities and the osmotically estimated molecular weights of these fractions and of the starting material have now been determined in acetone solutions. This

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate literature references at the end of this paper.
[3] The starting material from which the fractions were prepared had an acetyl content of 38.6 percent, an ash of 0.06 percent, a melting point of 250° C and a char point of 301° C.

paper, which presents the results of these measurements, shows tha for this type of acetate and within the range of chain lengths inve tigated, the system cellulose acetate in acetone does conform t Staudinger's rule; i. e., for this system the constant a has the valu unity in the relationship cited above.

II. METHODS

1. VISCOSITY MEASUREMENTS

The viscosity measurements were made in an Ostwald viscomete at 25°±0.03° C. As the time of efflux of the acetone was approx mately only 30 seconds, kinetic-energy corrections were applied [4] [5] These were determined by calibrating the viscometer with oils o known viscosity obtained at the National Bureau of Standards.

2. OSMOTIC-PRESSURE MEASUREMENTS

The osmotic-pressure values for all the fractions, except the one o lowest molecular weight, were determined by the dynamic method o Fuoss and Mead [6]. The denitrated cellulose nitrate membrane recommended by these authors were used. The measurements wer made at room temperature (approximately 28° C.). The cell wa placed in a box insulated with cotton waste, and the entire assembl was then covered with a wooden hood to minimize drifts caused b changes in temperature. Measurements of the osmotic pressure were made by means of a cathetometer sighted through a window i the hood. It was found practical to use the same membrane for a series of measurements by using increasing concentrations of the sam sample in successive measurements, as recommended by Fuoss an Mead [6]. The membrane was then rinsed thoroughly with aceton soaked overnight in this solvent, and rinsed thoroughly again, a without removing the membrane from the cell. This treatment su ficed to remove adhering cellulose acetate, so that the membran could be used again.

With the fraction of lowest molecular weight (15), and to a lesse extent with the starting material, appreciable diffusion of the solut through the denitrated cellulose nitrate membranes occurred. Fo these two samples, cellophane membranes, swollen with NH_4O according to the directions of Flory [2], were therefore used. Thes measurements were made by the static method in a constant-tem perature room. Equilibrium was reached overnight, after which n appreciable change in osmotic pressure occurred for a period of sever days.

As the osmotic pressure measurements were made at slightly di ferent temperatures, the values of $\overline{M}_n$ were calculated as follow The apparent value of $\overline{M}_n$ at each concentration (and correspondin temperature) was first calculated by using the van't Hoff relationship and the value of $\overline{M}_n$ at zero concentration was then obtained alge braically, assuming that the apparent value of $\overline{M}_n$ is a linear functio of concentration.

[4] Failure to apply kinetic energy corrections leads to errors of several percent in the values of the intrins viscosities of the fractions of higher molecular weight.

III. RESULTS AND DISCUSSION

The results of the viscosity measurements are presented in table 1 and shown graphically in figure 1. In this figure the values of η_{sp}/c are plotted on a logarithmic scale. When this procedure is followed, the results fall on straight lines suitable for extrapolation to zero concentration for obtaining the intrinsic viscosity. (When

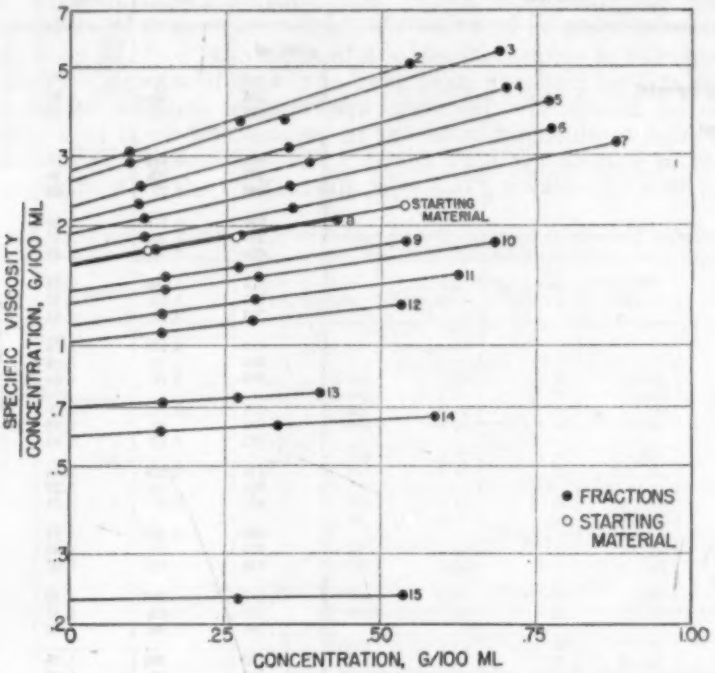

FIGURE 1.—*Viscosity-concentration relationship in acetone solutions for cellulose acetate samples.*

The samples are numbered in the order of their molecular weights to conform with their designations in a previous publication [4]. The lowest number represents the sample of highest molecular weight.

the values of η_{sp}/c and c are both plotted on a linear scale, the results do not fall on straight lines except at very low concentrations, where the experimental errors are largest. The use of the semilogarithmic plot gives weight to the more precisely determined values obtained in the range of higher concentrations).

The result of the viscosity measurements conform quite closely to Martin's equation [7]:

$$\log \frac{\eta_{sp}}{C} = \log [\eta] + k[\eta]\, C, \qquad (1)$$

in which C is the concentration,[5] and k is a constant characteristic of a given polymeric series in a given solvent. The values of $[\eta]$ given

[5] It should be noted that the concentration is expressed in g/100 ml of solution in the data presented here, whereas it is given in weight-percent in reference [7].

in table 1 were obtained by algebraic extrapolation, using the method of least squares.

TABLE 1.—*Viscosities of cellulose acetate samples in acetone solutions at 25° C*

[The samples are numbered in the order of their molecular weights to conform with their designations in a previous publication [4]. The lowest number represents the sample of highest molecular weight.]

Sample	Concentration	η_{sp}	η_{sp}/c	$[\eta]$
	g/100 ml			
Starting material	0.126	0.218	1.73	1.59
	.268	.50$_1$	1.87	
	.537	1.21$_0$	2.25	
Fraction:				
2	.094	0.259	3.08	2.75
	.273	.99$_9$	3.66	
	.546	2.77	5.08	
3	.096	0.278	2.90	2.59
	.345	1.27$_8$	3.71	
	.690	3.78	5.48	
4	.114	0.286	2.52	2.25
	.351	1.10$_3$	3.13	
	.703	3.12	4.43	
5	.110	0.251	2.28	2.05
	.384	1.10$_7$	2.88	
	.769	3.14	4.08	
6	.118	0.247	2.09	1.91
	.353	.89$_1$	2.52	
	.775	2.70	3.48	
7	.119	0.224	1.88	1.72
	.358	.79$_8$	2.22	
	.877	2.81	3.21	
8	.138	0.239	1.74	1.60
	.275	.52$_1$	1.89	
	.428	.88$_6$	2.07	
9	.152	.226	1.49	1.37
	.271	.42$_5$	1.57	
	.541	.98$_9$	1.82	
10	.152	.209	1.38	1.28
	.303	.45$_9$	1.49	
	.684	1.23$_6$	1.81	
11	.149	0.179	1.20	1.13
	.297	.385	1.30	
	.625	.94$_0$	1.50	
12	.147	.159	1.08	1.02
	.294	.338	1.15	
	.533	.67$_1$	1.26	
13	.149	.108	0.72	0.70
	.269	.199	.74	
	.403	.305	.76	
14	.147	.089	.61	0.59
	.335	.210	.63	
	.587	.390	.66	
15	.273	.063	.23$_1$	0.23
	.411	.097	.23$_6$	

The results of the osmotic-pressure measurements are given in table 2. Since it has been shown that a plot of the reduced osmotic pressure (π/c) against c gives straight lines for samples of cellulose acetate in acetone [8], the osmotic-pressure values were determined at only two concentrations for most of the samples. The slopes of the lines obtained by plotting π/c against c are very nearly identical for

all of the samples except the two fractions of lowest molecular weight (14 and 15), which give larger slopes.[6]

Figure 2 shows the relationship between the intrinsic viscosities and number-average molecular weights of the acetate fractions. The results appear to fall on a straight line passing through the origin, although the points for the two fractions of highest molecular weight appear to deviate somewhat from a line drawn through the remaining data. This deviation may be real, which would suggest that at higher values of molecular weight, the value of $[\eta]$ may increase less rapidly than $\overline{M}_n$ (i. e., the value of a is less than unity in the equation $[\eta]=KM^a$). Results of this type have been obtained by Gralen and Svedberg for cellulose in cuprammonium [3]. It should be noted, however, that these fractions cover the usual molecular-weight range of commercial cellulose acetates. If the data are treated as though they conform with the relationship $[\eta]=KM^a$, a value for a of 1.03 is

TABLE 2.—*Osmotic pressures of cellulose acetate samples in acetone solutions*

Sample	Concentration	Osmotic pressure	Temperature	Apparent $\overline{M}_n$	$\overline{M}_n$
	g/100 ml	*cm acetone*	*°C*		
Starting material	0.240	1.96	26	40,000	42,000
	.449	3.71	26	39,000	
	.837	7.19	21	37,000	
	.899	8.03	26	36,000	
Fraction:					
2	.259	0.67	26	126,000	130,000
	.547	1.47	24	121,000	
3	.345	1.10	28	102,000	110,000
	.690	2.37	28	95,000	
4	.351	1.37	27	84,000	86,000
	.703	2.83	27	81,000	
5	.384	1.71	30	74,000	78,000
	.769	3.59	30	71,000	
6	.388	1.82	30	70,000	76,000
	.775	3.98	31	64,000	
7	.439	2.49	32	59,000	62,000
	.877	5.33	33	55,000	
8	.428	2.44	24	57,000	61,000
	.855	5.27	25	53,000	
9	.136	0.85	28	52,000	53,000
	.182	1.15	28	52,000	
	.271	1.75	30	51,000	
10	.342	2.42	24	46,000	48,000
	.684	5.14	25	43,000	
11	.312	2.59	30	40,000	42,000
	.625	5.44	31	38,000	
12	.266	2.68	30	33,000	34,000
	.533	5.49	31	32,000	
13	.135	1.34	30	33,000	33,000
	.269	2.67	30	33,000	
14	.168	2.41	25	23,000	24,000
	.335	5.15	26	21,000	
15	.146	4.52	25	10,400	11,000
	.291	9.75	25	9,700	

[6] Fraction 15 diffused through the denitrated cellulose nitrate membranes of Fuoss and Mead [6]. When measurements were made by the dynamic method with these membranes, and the results were extrapolated back to zero time, the apparent value of $\overline{M}_n$ for fraction 15 was 16,000. The value of $\overline{M}_n$ when the less permeable swollen cellophane membranes were used was 11,000 (table 2).

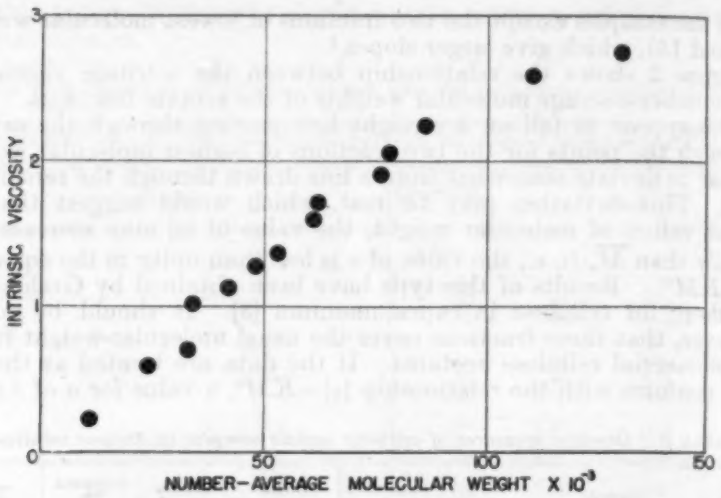

FIGURE 2.—*Relationship between intrinsic viscosity and osmotically estimated molecular weight for cellulose acetate fractions.*

obtained by the method of least squares. It should be noted that the value of a is very sensitive to the results obtained for the fractions of lower molecular weight. Moderately small errors in the results for these fractions might change the value for a appreciably.

From the best straight line drawn through the points in figure 2, the average relationship $\overline{DP}_n=150\ [\eta]$ [7] (where $\overline{DP}_n$ is the number-average degree of polymerization) is obtained.[8] The corresponding result obtained by Staudinger, who also used osmotic-pressure measurements to calibrate his viscosity method, is $\overline{DP}_n=110\ [\eta]$ [7] [1]. Kraemer measured the molecular weights of a series of secondary cellulose acetates by sedimentation equilibrium in the ultracentrifuge, and obtained the relationship $\overline{DP}_w=230\ [\eta]$ (where $\overline{DP}_w$ is the weight-average degree of polymerization) [9]. These results suggest that the cellulose acetate fractions used in this study are more homogeneous than those used by Staudinger, but that they are not sufficiently homogeneous so that their weight- and number-average DP's are equal. This is shown by the results in table 3.

Table 3 lists the number-average DP's of the fractions and starting material as obtained from the osmotic-pressure measurements in column 2. Column 3 lists the intrinsic viscosities, and column 4 the product $230[\eta]$, which according to Kraemer's results should approximate $\overline{DP}_w$. Since the ratio DP_w/DP_n is unity for a perfectly homogeneous polymer, and increases with the heterogeneity with respect to molecular size, the value of the ratio may be taken as a measure of this heterogeneity.[9] The values of this ratio for the

[7] It should be noted that this relationship holds only for fractions of this particular degree of homogeneity. Viscosity results properly should be related to weight-average or viscosity-average molecular weights rather than to number-average values. No estimate of $\overline{DP}_n$ can be obtained by viscosity measurements made on an unfractionated sample, or a fractionated sample of unknown degree of homogeneity.

[8] The weight per glucose residue of cellulose acetate of this degree of acetylation is 260 [4].

[9] Because of the uncertainty involved in applying Kraemer's constant to these samples, the ratios of $\overline{DP}_w/\overline{DP}_n$ should not be taken as absolute values. Measurements of $\overline{DP}_w$ for several of these samples by ultracentrifugal and light-scattering methods are in progress.

TABLE 3.—*Comparative DP_n's and intrinsic viscosity results for cellulose acetate samples*

Sample	$\overline{DP}_n$	[η]	230 [η]	$\frac{230\,[\eta]}{\overline{DP}_n}$
Starting material	160	1.59	366	2.3
Fraction:				
2	502	2.75	633	1.3
3	422	2.59	596	1.4
4	331	2.25	518	1.6
5	298	2.06	474	1.6
6	291	1.91	439	1.5
7	240	1.72	396	1.7
8	234	1.60	368	1.6
9	204	1.37	315	1.5
10	186	1.28	294	1.6
11	160	1.13	260	1.6
12	131	1.02	234	1.8
13	127	0.70	161	1.3
14	92	.59	136	1.5
15	43	.23	53	1.2

Several samples are shown in column 5. The starting material, with a ratio of $\overline{DP}_w/\overline{DP}_n$ of 2.3, is manifestly less homogeneous than any of the fractions, the ratios for which range between 1.2 and 1.8. The fact that the lowest value obtained for this ratio is slightly higher than unity is entirely consistent with Kraemer's results. However, the heterogeneity of all of the samples may be somewhat different from that indicated by these ratios, since the value of Kraemer's constant is subject to some uncertainty [9]. The results indicate that the samples have not all been fractionated to the same degree.

From the values in table 3 and the yields of the fractions, summated values of [η] and $\overline{DP}_n$ can be calculated. These calculated values are [η]=1.50 and $\overline{DP}_n$=175, compared with experimental values for the starting material of 1.59 and 160, respectively. Since the results do not include fraction 1, which was not completely soluble in acetone, and as a certain amount of loss is inevitable in a long fractionation procedure, the results represent reasonably good agreement between the calculated and observed values.

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POLYMOLECULARITY AND MECHANICAL PROPERTIES OF CELLULOSE ACETATE

By Arnold M. Sookne and Milton Harris [1]

ABSTRACT

The tensile strengths, ultimate elongations, and folding endurances of films prepared from a series of cellulose acetate fractions and blends were studied. When the mechanical properties are plotted against the intrinsic viscosities (or relative weight-average degrees of polymerization), the results for the fractions and different blends fall on separate curves. In contrast, when the mechanical properties are plotted against the number-average degrees of polymerization, the results for the fractions and all of the blends fall approximately on a single curve for each property. The results are shown to be qualitatively consistent with the hypothesis that the mechanical properties of blends are the weight-averages of the properties of their components. The results emphasize the importance of the determinations of the number-average degree of polymerization in studying commercial polymolecular materials.

CONTENTS

	Page
I. Introduction	467
II. Results and discussion	468
1. Mechanical properties as a function of intrinsic viscosity and number-average degree of polymerization	468
2. Additivity of mechanical properties	473
III. Conclusion	476
IV. References	476

I. INTRODUCTION

High polymers are in general polymolecular; that is, heterogeneous with respect to molecular size. The problem of the influence of the degree of polymolecularity on the mechanical properties of such materials is an important one, and it has received considerable study in recent years. The detailed results of these investigations are reviewed elsewhere [1, 2, 3][2]. The procedure generally followed in these studies was to fractionate a polymer with respect to molecular size, and compare the mechanical properties of the fractions with those of blends. There has been substantial agreement among the more recent investigators that fractionated cellulosic materials are superior in mechanical properties to blends of the same intrinsic viscosity; i. e., the same weight-average molecular weight [1, 4, 5]. In particular, it has been found that the presence of material of low

[1] Research Associates at the National Bureau of Standards representing the Textile Foundation.
[2] Figures in brackets indicate literature references at the end of this paper.

molecular weights exerts a harmful influence on the mechanical properties of blends. These results appear to be unambiguous only for unoriented or slightly oriented specimens; it is quite possible that other conclusions may be reached when oriented or crystallized materials are considered.

In an approach to this problem some time ago, a large quantity of commercial cellulose acetate was fractionated in this laboratory [6] and some of the mechanical properties of the fractions and their blends were studied [4]. It was found that these mechanical properties were more closely related to the number-average than to the weight-average DP's[3] of the samples. However, the $\overline{DP}_w$'s were at that time calculated from viscosity measurements at only one concentration (by means of Staudinger's rule), and the $\overline{DP}_n$'s of the blends were calculated under the assumption that the fractions were perfectly homogeneous. The $\overline{DP}_n$'s of the fractions have now been determined experimentally by osmotic pressure measurements in acetone solution, and their intrinsic viscosities have been determined in the same solvent [7]. It is the purpose of this discussion to re-examine the data for the mechanical properties of the fractions and blends in the light of these new measurements of $\overline{DP}_n$ and intrinsic viscosity. In addition, examination of the data shows that to a first approximation the mechanical properties of the blends are the weight-averages of the properties of their components; i. e.,

$$\text{Property}_{\text{blend}} = \frac{\Sigma w_i P_i}{\Sigma w_i}, \tag{1}$$

where w_i is the weight of the molecular species with a mechanical property P_i. It will be shown that the experimentally obtained relationships between the mechanical properties and the DP_n's and intrinsic viscosities are all consistent with this relationship.

II. RESULTS AND DISCUSSION

The separation of the fractions [6], measurement of the osmotic pressure values and intrinsic viscosities [7], and the preparation and mechanical testing of films of the fractions and blends [4] have been described in detail elsewhere.

1. MECHANICAL PROPERTIES AS A FUNCTION OF INTRINSIC VISCOSITY AND NUMBER-AVERAGE DEGREE OF POLYMERIZATION

Figure 1 shows the tensile strengths of the fractions as a function of their intrinsic viscosities (upper graph) and $\overline{DP}_n$'s (lower). In considering these and subsequent data (figs. 1 to 6), the intrinsic viscosity may be taken as a direct measure of $\overline{DP}_w$ on the basis of Kraemer's results [8] and because of the linear relationship between $\overline{DP}_w$ and $[\eta]$ (intrinsic viscosity) found for the fractions [7]. Because of the uncertainty in the value of Kraemer's constant, the data have been plotted as a function of $[\eta]$ rather than of $\overline{DP}_w$.[4] The curves have

[3] The weight-average and number-average degrees of polymerization will henceforth be written $\overline{DP}_w$ and $\overline{DP}_n$, respectively.

[4] The scale of the axis of abscissae in each upper graph of figures 1 to 6 has, however, been so adjusted that it compares directly with the DP axis of the lower graph, assuming $\overline{DP}_w = 230\,[\eta]$ (Kraemer's relationship

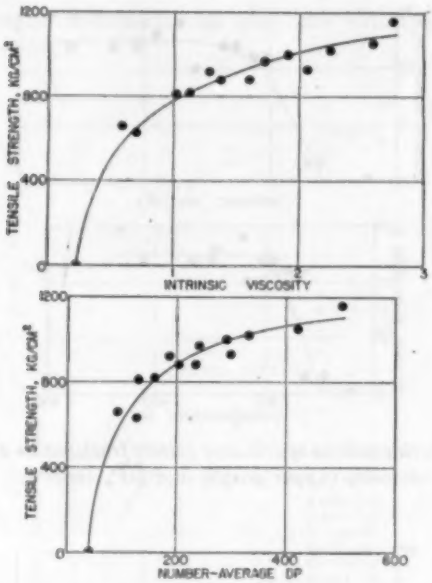

FIGURE 1.—*Tensile strengths of cellulose acetate fractions as a function of intrinsic viscosity (upper graph) and* $\overline{DP}_n$ *(lower).*

a large slope in the region of small chain length, followed by a gradually decreasing slope which may represent an approach to an asymptotic value for very high *DP*'s. Similarly shaped curves have been observed for numerous polymers [9]. The fraction of lowest chain length ($\overline{DP}_n$=43) was so brittle that it would not form a coherent film of sufficient size to be tested by ordinary technics, and it has therefore been assigned a strength of zero. Small fragments of this sample were tested by special technics, however, and a strength as high as 250 kg/cm² was obtained. This result suggests that the failure to obtain measurable strengths for this and other samples of very low *DP* results from the inadequacy of the film casting and testing technics, rather than from the weakness of the sample. Although it is true that such materials have zero strength as far as their practical utilization is concerned, the possibility exists that the curve relating strength to *DP* would pass through the origin if suitable testing technics were used.

Figure 2 shows the ultimate elongations of the fractions, plotted in the same manner as the tensile strength results. The shapes of the latter curves are generally similar to those for the tensile strength data, except that the approach to a limiting value is completed at a lower *DP* for the ultimate elongation results. As shown in figure 3, entirely analogous results were obtained for the measurements of the folding endurances of the fractions (made on a Massachusetts Institute of Technology Fold Tester).

In order to study the effect of distribution of chain length on mechanical properties, blends were prepared from pairs of the fractions. The major portion of the work on blends was done with three series, prepared by mixing in various proportions pairs of fractions of

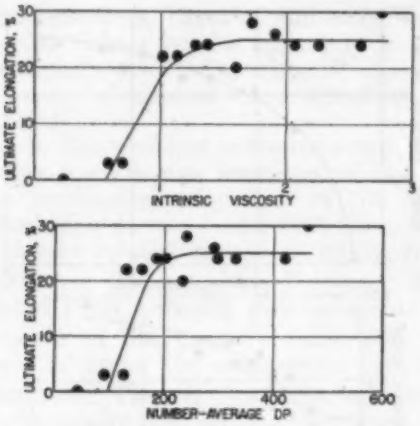

FIGURE 2.—*Ultimate elongations of cellulose acetate fractions as a function of intrinsic viscosity (upper graph) and* $\overline{DP}_n$ *(lower).*

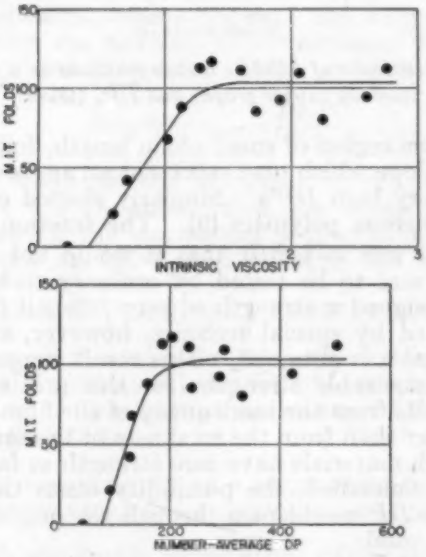

FIGURE 3.—*Folding endurances of cellulose acetate fractions as a function of intrinsic viscosity (upper graph) and* $\overline{DP}_n$ *(lower).*

the following $\overline{DP}_n$'s: 502+43, 502+127 and 502+204. (These same pairs of fractions are identified by their intrinsic viscosities of 2.75+.23, 2.75+.70, and 2.75+1.37, respectively.) A number of miscellaneous blends and the starting material were also studied. The intrinsic viscosities and $\overline{DP}_n$'s of the blends were calculated from

their known weight compositions and the intrinsic viscosities and $\overline{DP}_n$'s of the fractions.[5]

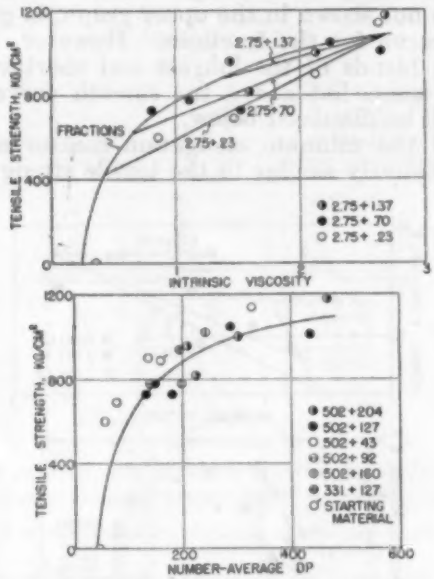

FIGURE 4.—*Tensile strengths of blends of cellulose acetate fractions as a function of intrinsic viscosity (upper graph) and $\overline{DP}_n$ (lower).*

The curve for the fractions (traced from fig. 1) is included for comparison.

Figure 4 shows the tensile strengths of the blends as a function of both their intrinsic viscosities (upper graph) and $\overline{DP}_n$'s (lower). The respective curves for the fractions, traced from the smooth curves of figure 1, are included for comparison. As shown by the upper graph of figure 4, the strengths of the blends are in general lower than those of the fractions when the results are plotted against intrinsic viscosity (or relative $\overline{DP}_w$). Further, the discrepancy between the curve for the fractions and that for a series of blends appears to increase with increasing difference in chain length between the components in a given series. Thus, the open circles, which represent blends of the longest and shortest chain lengths, fall farthest

[5] The intrinsic viscosities of the blends were calculated from the formula

$$[\eta]_{blend} = f_1[\eta]_1 + f_2[\eta]_2,$$

where f_1 and f_2 are the weight fractions in the blend of the components of intrinsic viscosities $[\eta]_1$ and $[\eta]_2$, respectively. The values of $\overline{DP}_n$ for the blends were obtained from the relationship

$$\overline{DP}_{n_{blend}} = \frac{1}{\frac{f_1}{\overline{DP}_{n_1}} + \frac{f_2}{\overline{DP}_{n_2}}},$$

where f_1 and f_2 are the weight fractions in the blend of the components of $\overline{DP}_{n_1}$ and $\overline{DP}_{n_2}$, respectively.

Calculated rather than experimental values of $[\eta]$ and $\overline{DP}_n$ for the blends were used because of the unquestioned validity of the calculation procedure, and because samples of the original blends sufficient for the experimental measurements were not available.

below the curve for the fractions. In contrast, when the tensile strengths are plotted against $\overline{DP}_n$ (lower graph, fig. 4), the results for the blends, including the starting material and a number of miscellaneous blends not shown in the upper graph, in general fall closer to the smooth curve for the fractions. However, the open circles (which represent blends of the longest and shortest chain lengths) fall consistently somewhat above the smooth curve. The possible cause for this will be discussed below.

The results of the ultimate elongation measurements on blends (fig. 5) are qualitatively similar to the tensile strength data, but the

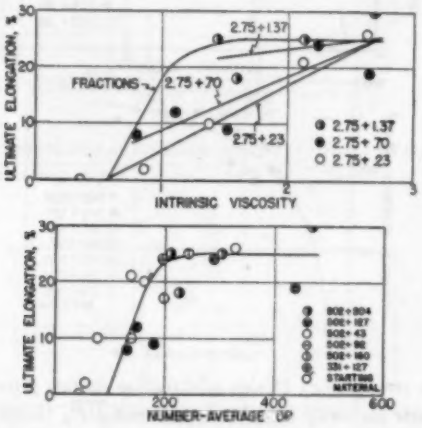

FIGURE 5.—*Ultimate elongations of blends of cellulose acetate fractions as a functio of intrinsic viscosity (upper graph) and* $\overline{DP}_n$ *(lower).*

The curve for the fractions (traced from fig. 2) is included for comparison.

differences between the upper and lower graphs are more clearly defined. In the upper graph, the curves for the blends of fraction of intrinsic viscosities 2.75+.23 fall markedly below the smooth curv for the fractions (traced from fig. 2), the results for the series 2.75+.7 are intermediate, and those for the series 2.75+1.37 are quite clos to the curve for the fractions. In the lower graph, in which th results are plotted against $\overline{DP}_n$, all of the results for the blends fa fairly close to the curve for the fractions; the open circles, however again consistently fall somewhat above the smooth curve.

The results for the folding endurance measurements (fig. 6) ar analogous to those for the ultimate elongations. The difference between the blends and fractions are again large when the results ar plotted against intrinsic viscosity. The results for the series 2.75+ 1.37 appear to fall somewhat above the smooth curve for the frac tions, but it is possible that this difference results from the variabilit inherent in folding endurance measurements rather than any actua superiority of the blends. As shown by the lower graph of figure 6 the results for all the blends once more fall fairly close to the curve fo the fractions when $\overline{DP}_n$ is taken as the independent variable. Again however, the results for the series $\overline{DP}_n$'s 502+43 (open circles) fa slightly above the curve for the fractions.

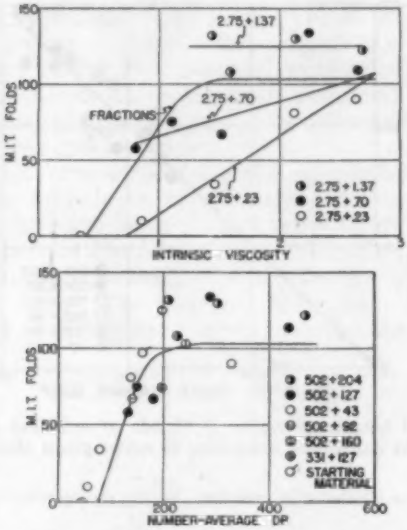

FIGURE 6.—*Folding endurances of blends of cellulose acetate fractions as a function of intrinsic viscosity (upper graph) and* $\overline{DP}_n$ *(lower).*

The curve for the fractions (traced from fig. 3) is included for comparison.

2. ADDITIVITY OF MECHANICAL PROPERTIES

The results described above demonstrate that the mechanical properties of blends are more closely related to $\overline{DP}_n$ than to $\overline{DP}_w$. It can be shown that this closer relationship between mechanical properties and $\overline{DP}_n$ is consistent with two factors: the shape of the curve relating mechanical properties to *DP* for the fractions, and the fact that the mechanical properties of a blend are the weight-averages of the properties of their components (eq 1). The second point will be considered first.

Examination of the tensile strength data for the blends reveals that if a strength of approximately 260 kg/cm² is assigned to the fraction of lowest *DP*, for which no precise experimental value could be obtained, the strength of each blend is the weight-average of the strengths of its components. This is shown in figure 7, in which the observed strength of each blend has been plotted against the value calculated (according to eq 1) from the weight percentages and strengths of the fractions of which it is composed. A line of 45-degree slope passing through the origin is included in the figure for comparison. The one blend which departs seriously from the line (observed strength, ; calculated strength, 310) was a 95:5 mixture by weight of the fractions of shortest and longest chain lengths, respectively. This blend, like the fraction of lowest *DP*, was too brittle to give a film suitable for testing.

A similar relationship between the observed and calculated ultimate elongations of the blends can also be demonstrated, but because of the lower precision of these results, the agreement between the observed and calculated values is not so good as for the tensile strength measurements. The folding endurances of all the blends except those contain-

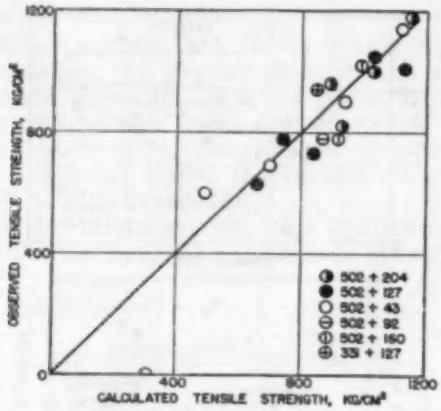

FIGURE 7.—*Observed tensile strengths of blends of cellulose acetate fractions as a function of strengths calculated according to assumption that strengths of fractions are additive (eq 1).*

The 45° line is included for reference. For complete description, see text.

ing the fraction of smallest chain length ($\overline{DP}_n$=43) are also approximately additive. For the latter blends, the folding endurance values are additive only if the fraction with a $\overline{DP}_n$ of 43 is assumed to have a negative folding endurance. This somewhat unreasonable result is, however, consistent with the shape of the curve relating folding endurance to $\overline{DP}_n$ for the fractions (fig. 3), as extrapolation of this curve to a $\overline{DP}_n$ of 43 would lead to a negative folding endurance.

It is now of interest to examine the consequences of applying the concept of additivity of mechanical properties to curves relating such properties to chain length for fractionated materials. For this purpose, the curve shown in figure 8 was chosen. It should be emphasized, however, that the results described below would be qualitatively similar if any of the experimental curves of figures 1 to 3 were used in this discussion. Figure 8 is a theoretical curve calculated from the equations of Sullivan [10], relating strength and fiber length of yarns which are perfectly homogeneous with respect to fiber

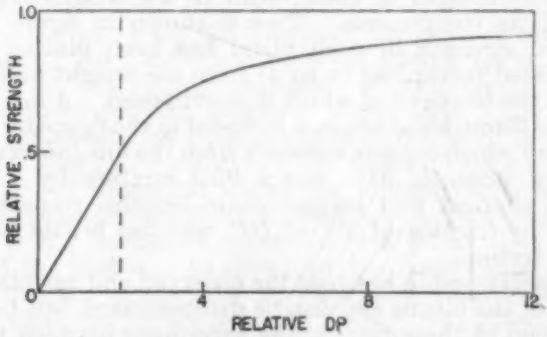

FIGURE 8.—*Theoretical curve, relating strength to DP for perfectly homogeneous polymers.*

length.[6] It differs qualitatively from typical experimental curves only in that it passes through the origin. As suggested above, however, the failure of the experimental strength-*DP* curves to pass through the origin may well result from technical difficulties in film preparation and testing. In any case, this difference does not seriously affect the conclusions drawn below.

Figure 9 shows the strengths of blends, calculated from the curve of figure 8, assuming additivity of strength. As in the experimental curves, the strengths have been plotted on both weight- and number-average bases. Results for four series of blends have been plotted, representing varying proportions of the following pairs: 4+10, 2.5+10, 1+10, and .01+10. The numbers have been so chosen that the first three of these approximately represent the three series of blends

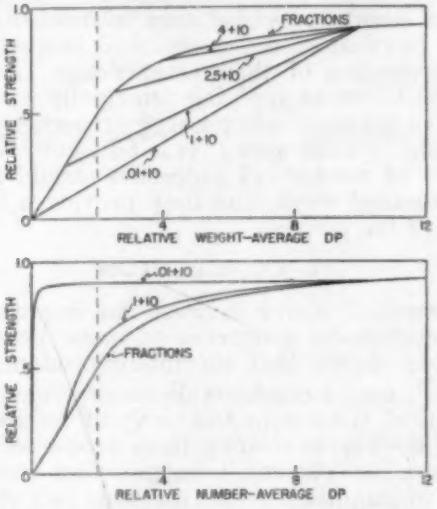

FIGURE 9.—*Theoretical curves, relating strength to* $\overline{DP}_w$ *(upper graph) and* $\overline{DP}_n$ *(lower) for blends of homogeneous polymers.*

The curve for the fractions is identical with that given in figure 8. See text for complete explanation.

studied experimentally, and the last is roughly equivalent to blends of the fraction of highest *DP* and a monomer. As shown by the upper graph of the figure, when the results are plotted on a weight-average basis, the calculated strengths of the blends fall on straight lines below the curve for the fractions. The extent of the departure from the curve for the fractions increases with the disparity between the chain lengths of the components in a pair. In contrast, when the results are plotted on the number-average basis, the curves for the blends of pairs 4+10 and 2.5+10 fall directly on the curve for the fractions. The curve for the pair 1+10, which corresponds to the

[6] According to Sullivan's analysis [10], to the left of the broken line in figure 8, yarn breakage occurs solely by slippage of the fibers. As the strength is contributed solely by frictional forces in this range, it is directly proportional to fiber length. To the right of the broken line, the frictional forces are sufficiently large to cause some fiber breakage, and the strength approaches asymptotically to a maximum value at which all fibers break. The analogy between frictional forces between fibers in a yarn and interchain forces in a film or filament is fairly close, but it is not suggested that the breaking in tension of a film can be explained in terms of this analysis. Thus, the breaking of a film includes a complex process of flow and crystallization, for which there is no counterpart in a yarn. The two processes do, however, contain a number of interesting points of similarity.

experimental blends of the longest and shortest chain lengths, falls slightly above the curve for the fractions, as did the open circles in the lower graphs of figures 4, 5, and 6. The curve for the pair .01+10, however, falls far above the curve for the fractions, which result is also in accord with experience [3]. Thus, these curves, which merely represent a statement of the weight-additivity of the strength, reproduce all of the features of the experimental data. It is perhaps worth noting that the series 1+10 (and the corresponding experimental series, as well) contains blends considerably more heterogeneous than the common unplasticized commercial polymers. Thus, some of the blends in this series have a ratio of $\overline{DP}_w/\overline{DP}_n$ higher than 3, as compared with a value of about 2 for most ordinary polymers. Even for this series, however, the mechanical properties are much more closely related to $\overline{DP}_n$ than to $\overline{DP}_w$.

The discussion above provides only a limited and qualitative approach to the problem of the mechanical properties of blends as related to the properties of their components. Further, the conclusions should be taken as applying principally to strength properties, rather than to the more complicated properties such as ultimate elongation and folding endurance. It is felt, however, that the concept of additivity of mechanical properties should prove helpful in some types of practical work, and may provide a basis for a more detailed analysis of the problem.

III. CONCLUSION

The results described above indicate the importance of $\overline{DP}_n$ in considering the mechanical properties of linear polymolecular polymers. It has been shown that the interdependence of mechanical properties and $\overline{DP}_n$ over a considerable range of chain lengths can be explained in terms of the weight-additivity of mechanical properties, and the shape of the curves relating these properties and the *DP* for fractionated materials. The results suggest that further attention be given to the use of osmotic pressure methods and other methods for determining $\overline{DP}_n$ in industrial work.

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